Study of the synergistic effect of plant-derived and synthesized inhibitor systems against corrosion

G.R. Gurbanov,[1]* S.M. Pashayeva,[1] G.M. Talybov,[2] N. Shirinova,[2] I. Ozdemir[3] and Z.Y. Xin[4]

[1]Department of Oil and Gas Transportation and Storage, Azerbaijan State Oil and Industry University, Baku, Azadlig Avenue 20, AZ1010, Azerbaijan
[2]Department of Chemical Technology, Recycling and Ecology, Azerbaijan Technical University, Baku, G. Javid Avenue 25, AZ1073, Azerbaijan
[3]Catalysis Research and Application Centre, Inonu University, Malatya, Elazig Road 15, 44280, Turkey
[4]Xuxin Trading Co., Ltd., Dongguan, Guangdong Province, Guanzhang Road 18, 523000, China
**E-mail: azii2009@mail.ru*

Abstract

In this research work, the preparation of multifunctional compositions based on green inhibitors for multicomponent aggressive corrosion environments (H_2S, CO_2, their combined effect and sulfate-reducing bacteria) widespread in the oil and gas industry and a comprehensive experimental evaluation of their corrosion protection properties were carried out. Within the framework of the research, an inhibitor system based on plant-derived Gossypol resin and a newly synthesized organic compound with the conditional name “Marza-3” was studied. The corrosion rate was determined by the gravimetric method in a model produced water environment saturated with H_2S and CO_2, as well as in the coexistence of these gases. In addition, the effect of the prepared compositions on the activity of sulfate-reducing bacteria (*Desulfovibrio desulfuricans* and *Desulfomicrobium*) and the formation of biogenic hydrogen sulfide was also investigated. The results obtained showed that the compositions obtained by combining the components in an equimolar ratio (1:1) showed a high protective effect, reducing the corrosion rate by 96–99%, and at the same time weakening the activity of SRB bacteria by 94–98%. A strong statistical relationship (R^2=0.947) was established between corrosion inhibition and the reduction of biogenic H_2S. The results prove that the proposed inhibitor systems simultaneously affect the electrochemical and microbiological corrosion mechanisms, reducing their intensity, and in this regard can be considered promising for application in the oil and gas industry.

Received: April 10, 2026. Published: May 22, 2026 doi: 10.17675/2305-6894-2026-15-2-17

Keywords: *carbon dioxide, sulfate-reducing bacteria, gossypol resin, Marza-3, microbiological corrosion, synergistic effect.*

1. Introductıon

In the oil and gas industry, pipelines, tanks and various technological facilities are operated under the influence of aggressive environments. Hydrogen sulfide (H_2S), carbon dioxide (CO_2) and sulfate-reducing bacteria (SRB) present in such environments cause the development of complex and multi-component corrosion processes on metal surfaces. In these environments, carbon dioxide corrosion, sulfide corrosion, and microbiological corrosion occur in parallel. In particular, biogenic H_2S formed as a result of the activity of SRB forms iron sulfides on the metal surface, leading to the formation of local corrosion foci and the development of pitting-type damage. In addition, H_2S and CO_2 accelerate the electrochemical dissolution processes of the metal and facilitate the diffusion of atomic hydrogen into the crystal lattice of the metal, promoting dangerous phenomena such as hydrogen embrittlement and sulfide corrosion cracking [1–5]. Currently, one of the most widely used methods in the fight against corrosion is the use of inhibitors. This approach is distinguished by its technological simplicity, economic efficiency, and the absence of additional structural changes to existing systems. Corrosion inhibitors of organic origin, especially compounds containing heteroatoms (O, N, S and P) in the molecule, adsorb on the metal surface and form stable metal-organic complexes as a result of donor-acceptor interactions. These complexes create a protective barrier between the metal surface and the aggressive environment, weakening the kinetics of both anodic and cathodic reactions and significantly reducing the overall corrosion rate [6–9]. In recent years, against the backdrop of tightening environmental requirements and the actualization of sustainable development strategies, interest in “green inhibitors” of natural origin has increased significantly. Plant extracts are widely studied as an alternative to synthetic inhibitors due to their low toxicity, biodegradability and economic feasibility [10–12]. Literature data show that various plant extracts demonstrate high effectiveness against corrosion of low-carbon steel in acidic environments, including H_2S, CO_2 HCl and H_2SO_4 solutions [13–16]. Plant extracts are selected for their low toxicity and biodegradability and are evaluated as a promising alternative in corrosion protection. The effectiveness of these systems is mainly explained by the interaction of phenolic and heteroatom-containing functional groups with the metal surface [10–16]. On the other hand, in most of the existing studies, inhibitor systems have been studied separately from the perspective of either electrochemical corrosion or microbiological corrosion. The synergistic effect and multifunctional nature of inhibitors for multicomponent environments where H_2S, CO_2 and SRB are simultaneously present have not been sufficiently investigated. In particular, information on the complex protective mechanisms resulting from the combination of naturally occurring phenolic substances, such as Gossypol, with synthetic organic compounds is limited. This scientific gap necessitates the development of new generation, multifunctional and environmentally safe inhibitor systems [17–20]. In this regard, in the presented study, the anti-corrosion effectiveness of the inhibitor system prepared based on the combination of the newly synthesized heterocyclic compound (1*R*,2*R*)-2-(1*H*-indol-3-yl)-2-phenyl-1-[(prop-2-yn-1-yl)oxy]ethan-

1-ol (common name “Marza-3”) with Gossypol resin was investigated for the first time in a comprehensive manner. The π-electron systems, heteroatoms and functional groups present in the structure of the Marza-3 molecule provide its strong adsorption capacity to the metal surface, while Gossypol exhibits additional complexing, antioxidant and potential bactericidal properties due to its phenolic structure.

The main objective of the study is to prepare a new multifunctional inhibitor system based on Marza-3 and Gossypol resin, to comprehensively evaluate its effect on corrosion processes in aggressive environments with the presence of H_2S, CO_2 and SRB, and to explain its protective mechanism.

It should be noted that phenomena such as hydrogen embrittlement and sulfide stress cracking are mentioned here as part of the general corrosion mechanisms reported in the literature. The present study is focused on the evaluation of corrosion rate and inhibition efficiency under the investigated conditions, and does not include a direct assessment of mechanical degradation mechanisms such as hydrogen embrittlement or sulfide stress cracking.

2. Experimental Details

2.1. Corrosion testing – gravimetric method

Corrosion tests were conducted using the gravimetric method in a simulated MI formation water. The chemical composition of MI (g/l): NaCl – 17.0; $NaHCO_3$ – 0.8; $MgCl_2 \cdot 6H_2O$ – 0.2; $CaCl_2$ – 0.2. The medium was saturated with H_2S and CO_2 separately and together. CO_2 was charged to 1 atmosphere through a high-pressure cylinder and monitored with a manometer. H_2S was obtained from the reaction of an equivalent amount of sodium sulfide with hydrochloric acid in the medium, and its amount was determined by iodometric titration [21, 22]. H_2S tests were conducted in 1-liter closed containers, and CO_2 tests were conducted in 0.5-liter plastic containers. The experiments were performed according to the ASTM G31 72 standard [23]. The tests were conducted on steel samples made of Ct3 brand, measuring 30×20×1 mm. All samples were polished with sandpaper, degreased in acetone, washed with anhydrous ethanol and dried. Finally, the samples were sterilized under ultraviolet (UV) irradiation for 30 minutes before use. The experiments were carried out at a temperature of 298 K and the mass loss occurring within 6 hours for each case was taken as the total mass loss. Based on the average mass loss (average value of three parallel experiments), the metal corrosion rate (*CR*) and the inhibitor effectiveness (*Z*%) were calculated using the following:

$$CR = \frac{\Delta W}{A \cdot t}$$

where ΔW is the mass loss, A is the surface area of the sample (m^2), t is the time the sample is in the environment (min).

$$Z(\%) = \frac{(CR_0 - CR_{inh})}{CR_0} \cdot 100$$

where CR_{inh} represents the corrosion rate in the presence of the inhibitor, and CR_0 represents the corrosion rate in the blank medium without the addition of the inhibitor.

All experiments were conducted at a constant temperature of 298 K. Temperature variation was not considered in this study, as the primary objective was to evaluate the inhibitor performance under controlled laboratory conditions.

2.2. Inhibitor characterization

In the preparation of new compositions, a mixture of Gossypol resin and a new organic compound (1*R*,2*R*)-2-(1*H*-indol-3-yl)-2-phenyl-1-[(prop-2-yn-1-yl)oxy]ethan-1-ol, conventionally called Marza-3, was used. Gossypol resin is a green inhibitor that is an intermediate product of cottonseed oil production [23]. Diesel fuel and kerosene fuels were used as solvents in Gossypol resin. It was found that the ratios of diesel and kerosene to Gossypol reduce the freezing point of the obtained solution to different degrees, and this decrease is reflected in Figure 1 below.

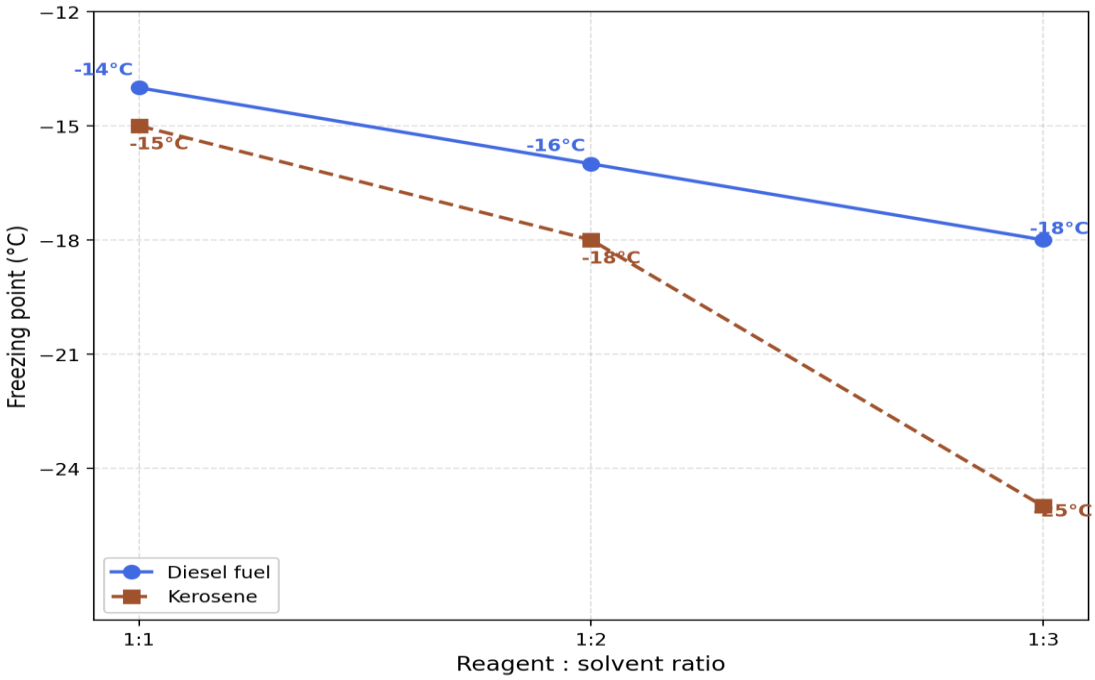


Figure 1. Dependence of the freezing point of gossypol resin on the type and ratio of solvent.

As can be seen from the figure, the freezing point decreases as the amount of solvent increases. The lowest freezing point is observed in a 1:3 mixture with kerosene (–25°C).

2.3. Synthesis of (1R,2R)-2-(1H-indol-3-yl)-2-phenyl-1-[(prop-2-yn-1-yl)oxy]ethan-1-ol, conventionally called "Marza-3"

To a flame-dried two-neck flask under a nitrogen atmosphere, 3 mL of anhydrous CH_2Cl_2, (*R*)-1,1′-bi-2,2′-naphthotitanium diisopropoxide (5.5 mg, 0.015 mmol), and 2.25 mmol of

substituted indole were added. The reaction mixture was stirred for several minutes, after which 1.5 mmol of unsaturated aromatic epoxide was introduced.

The resulting clear solution was stirred at room temperature until complete consumption of the epoxide (8–16 hours), as monitored by GC. The reaction mixture was then quenched with saturated $NaHCO_3$ solution and extracted with diethyl ether (Et_2O). The organic layer was dried over Na_2SO_4, concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica gel.

2.3.1. General methods

Chemical shifts in the ^1H NMR spectra are reported in δ (ppm) relative to tetramethylsilane (TMS) as an internal standard. Coupling constants (*J*) are given in hertz (Hz). Data are presented as follows: chemical shift, multiplicity (*s*=singlet, *d*=doublet, *t*=triplet, *q*=quartet, *br*=broad, *m*=multiplet).

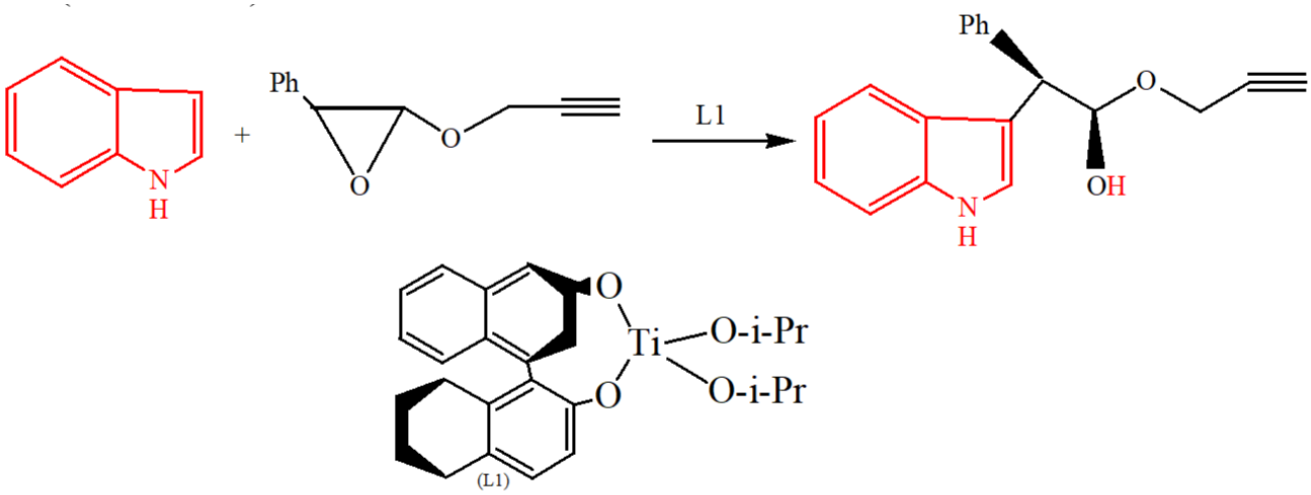
^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm relative to TMS, using the solvent as an internal standard ($CDCl_3$: δ 77.0 ppm; DMSO-d_6: δ 39.0 ppm).

After removal of the solvent, the residue was purified by column chromatography on silica gel using petroleum ether as the eluent.

Elemental analysis was performed using a CHNOS analyzer. Infrared (IR) spectra were recorded using a Sapphire-ATR spectrophotometer, and absorption bands are reported in cm^{-1}.

High-performance liquid chromatography (HPLC) was carried out on a liquid chromatograph equipped with a Daicel Chiralcel OD column (0.46 cm×25 cm i.d., Daicel Inc.).

Optical rotations were measured in a 1 mL cell with a 10 mm path length, using the sodium D-line (Na D-line).



(R)-1,1'-bi-2,2'-naphthotitanium diisopropoxide

(1*R*,2*R*)-2-(1*H*-indol-3-yl)-2-phenyl-1-[(prop-2-yn-1-yl)oxy]ethan-1-ol (1): White solid. Yield 78%; M.W.=237/30; R_f 0.41 (cyclohexane/AcOEt 75:25); m.p. 115–116°C; $[\alpha]^{25}_D$=+46.8 (c 1.6, $CHCl_3$); ee=96% by HPLC: isocratic 80/20 n-hex/IPA, t_S=9.3 min, t_R=10.6 min. ^{1}H NMR (300 MHz, $CDCl_3$), *d*: 7.79 (*br*, NH), 7.47–7.01 (*m*, 9H), 5.61 (*m*, 1H), 4.45 (*d*, *J*=6.6 Hz, 1H), 4.08 (*d*, ^4J=2 Hz, $OCH_2C\equiv$, 2H), 3.89 (*d*, *J*=6.6 Hz, 1H), 2.55 (*t*, ^4J=2 Hz, ≡CH, 1H), 1.61 (*br*, 1H). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 142.52, 135.32, 128.47 (2), 128.16 (2), 126.82, 126.63, 122.92, 121.81, 119.41, 119.24, 115.81, 111.08, 80.75 (OCH), 75.13 (°C*-CH_2O), 69.42 (°CH), 66.32, 56.03 (°C-*CH_2O). IR (ATR):3504, 3415, 3287, 3245, 2110, 1614, 1600, 1483, 1340, 1108, 1040, 1015, 701 cm^{-1}. Found, %: C 78.31; H 5.76; N 4.76. $C_{19}H_{17}NO_2$. Calculated, %: C 78.33; H 5.88; N 4.81.

2.4. Study of bactericidal properties

For the study, *Desulfovibrio desulfuricans* (DvD) and *Desulfomicrobium* (Dsm) strains taken from the produced waters of SOCAR's Bibiheybat field were used. These bacteria were grown in Postgate medium. The chemical composition of the Postgate medium is presented in Table 1 and the pH value was adjusted to 7.0±0.1 [24].

Table 1. Chemical composition of Postgate medium (g/l).

Component	**KH_2PO_4**	**NH_4Cl**	**Na_2SO_4**	**$CaCl_2$**	**$MgSO_2$**	**Na-lactate**	**pH of the liquid**	**Ascorbic acid (1% Na_2SO_3 in 5% solution)**
Postgate	0.5	1.0	1.0	0.06	0.06	6.0 ml	7.0	0.1 q

The amount of biogenic hydrogen sulfide was determined spectrophotometrically. During the analysis, sulfide ions were converted into a methylene blue complex in the presence of *N*,*N*-dimethyl-*p*-phenylenediamine and $FeCl_3$ in an acidic medium. The optical density of the resulting solution was measured in a UV-Vis spectrophotometer at a wavelength of 665 nm. The amount of H_2S was calculated based on a calibration curve constructed using previously prepared Na_2S standard solutions.

The bactericidal effect of the reagent (*S*%) according to the amount of hydrogen sulfide is calculated by the following:

$$S,\% = \frac{C_0 - C_{\text{inh}}}{C_{\text{inh}}} \cdot 100$$

where, C_0 – the concentration of biogenic hydrogen sulfide in the environment without reagent, C_{inh} – the concentration of biogenic hydrogen sulfide in the environment with reagent.

The coefficient of variation of the concentration of hydrogen sulfide (γ_c) is calculated by the following:

$$\gamma_c = \frac{c_{(H_2S)_0}}{c_{(H_2S)_{inh}}}$$

where $c_{(H_2S)_0}$ is the concentration of hydrogen sulfide in the medium without reagent; $c_{(H_2S)_{inh}}$ is the the concentration of hydrogen sulfide in the medium with reagent.

2.5. Statistical processing

All experimental measurements were performed in at least three parallel replicates and the results are presented as mean ± standard error. The statistical validity of the data was assessed by Student's *t*-test and one-way analysis of variance (ANOVA). Statistical differences were considered significant at the $p < 0.05$ level. Correlation and regression analyses were performed using OriginPro software.

3. Results and Discussion

3.1. Gravimetric tests

3.1.1. Determination of optimal composition

The interaction of components in a combined inhibitor system is one of the main factors determining its anti-corrosion effectiveness. Therefore, first of all, the protective effectiveness of mixtures of Marza-3 and Gossypol resin in different proportions was evaluated by the gravimetric method. The experiments were carried out in a 3.5% NaCl solution for 6 hours.

The experiments in this section were performed in a 3.5 wt.% NaCl solution at 298 K for 6 hours under atmospheric conditions. This medium was selected as a simplified model electrolyte to preliminarily evaluate the interaction and optimal ratio of inhibitor components under controlled laboratory conditions.

It should be noted that corrosive environments containing H_2S, CO_2, and their combination (H_2S+CO_2) were not applied at this stage. These aggressive media were investigated separately in Section 3.1.2 to evaluate the inhibitor performance under conditions simulating real oilfield environments.

The use of 3.5% NaCl solution at this stage was intended for preliminary screening of inhibitor performance under simplified and controlled conditions. Further experiments were conducted in model MI formation water to evaluate the inhibitor behavior under more realistic oilfield conditions. The ratio of Marza-3: Gossypol resin was changed from 0:100 to 100:0 with a 10% increase, and the protective effectiveness was determined for each composition. The results obtained are presented in Table 2, and the graphical interpretation of this dependence is presented in Figure 2. It should be noted that solutions of Gossypol in diesel and kerosene were used in the experiment. The total amount of the mixture was 120 g/L.

Table 2. Protective effect of different ratios of Marza-3 and Gossypol resin.

Marza-3 (%)	Gossypol resin (%)	*Z*% (diesel solvent)	*Z*% (kerosene solvent)
10	90	84.0	82.0
20	80	86.0	84.0
30	70	88.0	86.0
40	60	90.0	88.0
50	50	95.0	94.0
60	40	93.0	91.0
70	30	91.0	89.0
80	20	90.0	88.0
90	10	89.5	87.5

As can be seen from the table data, the efficiency gradually increases as the percentage of components in the mixture changes and reaches a maximum value (*Z*=94 and 95%) at a ratio of 50:50. Based on the results of this study, two compositions were selected. Composition-1 (Marza-3 + Gossypol in diesel solvent = 1:1 ratio), Composition-2 (Marza-3 + Gossypol in kerosene solvent = 1:1 ratio).

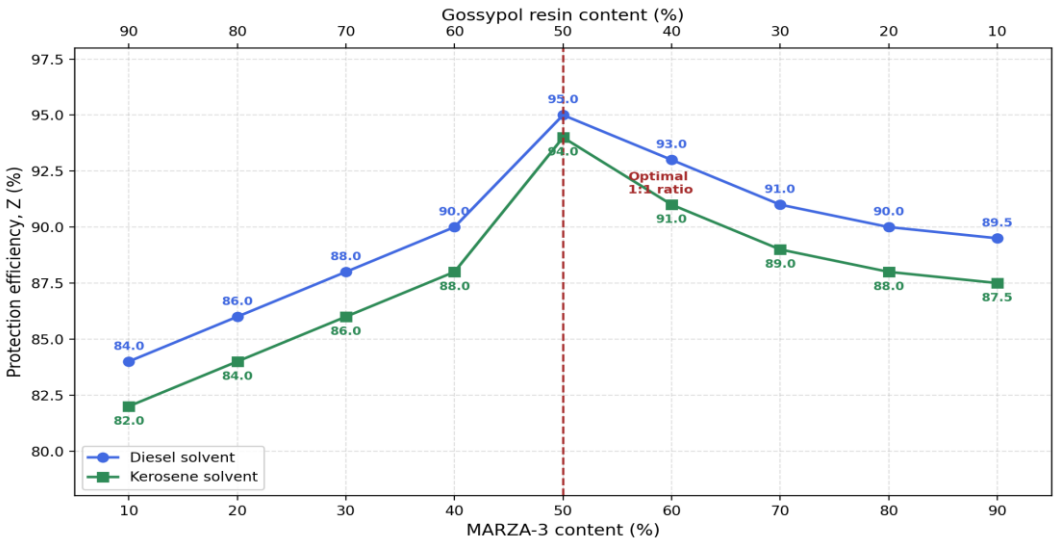


Figure 2. Dependence of the protective effect on the ratio of Marza-3: Gossypol resin.

The graph presented in Figure 2 clearly shows that the protective efficiency varies depending on the ratio of components. The efficiency increases rapidly up to a ratio of 1:1, and then decreases as the share of Marza-3 or Gossypol resin increases. This indicates that the optimal inhibitor system has maximum stability in a certain composition interval. Although the results obtained in the kerosene solvent are 1–2% lower than in the diesel

variant, the general trend does not change and a high efficiency ($Z \sim 94\%$) is maintained at a ratio of 1:1.

The change in the mass loss of the St-3 steel sample with and without the presence of mixtures prepared on the basis of Marza-3 and Gossypol resin in NaCl solution is shown in Figure 3.

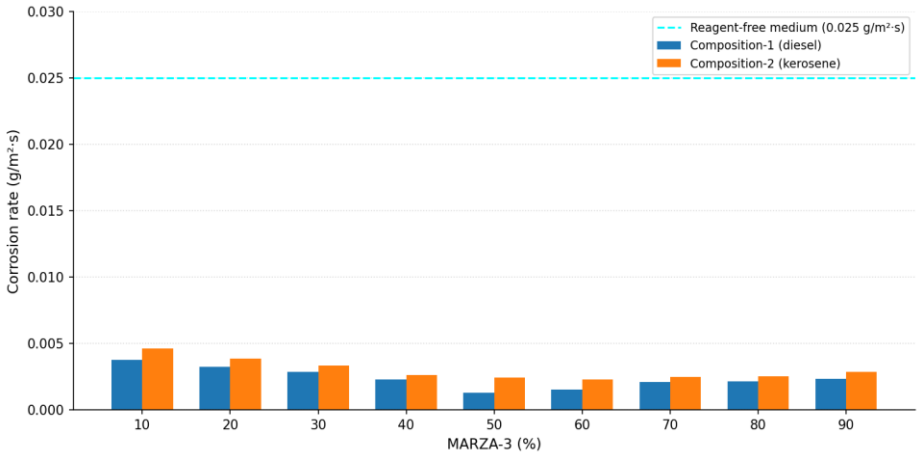


Figure 3. Corrosion rate of St-3 steel in reagent-free and reagent-containing environments.

The reagent-free condition (0.025 g/m^2·h) shown by the dashed line in Figure 3 allows for a visual comparison of the effectiveness of all compositions. The minimal mass loss observed at the optimal composition (50:50 ratio) confirms the high protective capacity of the inhibitor system. Overall, the results obtained show that Composition-1 and Composition-2, prepared on the basis of Marza-3 and Gossypol resin, effectively attenuate the corrosion of St-3 steel in chloride-containing environments, minimizing mass loss.

3.1.2. Determination of the protective efficacy of Marza-3 and Gossypol resin in H_2S, CO_2 and H_2S+CO_2 environments

In order to conduct a comparative analysis, the corrosion protection properties of the components of the compositions were studied in three main corrosion environments commonly encountered in the oil industry: H_2S, CO_2 and H_2S+CO_2. Marza-3 inhibitor was prepared in concentrations of 5, 10, 15 and 20 mg/l, and Gossypol resin was prepared in diesel fuel and kerosene solvents and studied in concentration intervals of 50, 100, 150 and 200 mg/l. The effectiveness of the inhibitors (Z%) was determined depending on the concentration and the results obtained are presented in Table 3. For completeness, the corrosion rate in the uninhibited (blank) medium was determined for all investigated environments. The corrosion rate in the H_2S-containing medium was 0.98 g/m^2·h, while in the CO_2-containing medium it was 0.76 g/m^2·h. The highest corrosion rate was observed in the combined H_2S+CO_2 environment, reaching 1.20 g/m^2·h.

These results indicate a more aggressive corrosion behavior in the mixed gas environment, confirming the synergistic effect of H_2S and CO_2 on the corrosion process.

Table 3. Protective efficacy of inhibitors in different environments.

Concentration (mg/l)	H_2S	CO_2	H_2S+CO_2
Marza-3			
5	43	39	47
10	56	53	62
15	74	71	76
20	87	84	92
Gossypol resin – in diesel solvent			
50	62	58	68
100	78	74	83
150	83	80	88
200	86	82	90
Gossypol resin – in kerosene solvent			
50	60	56	64
100	75	70	80
150	80	77	85
200	84	80	88

The results of Table 3 show that for all the inhibitor systems studied, the inhibitory efficiency increases consistently with increasing concentration, and this increase shows a similar trend in all corrosion media (H_2S, CO_2 and H_2S+CO_2). Marza-3 shows the highest efficiency even at low concentrations, increasing to 92% in H_2S+CO_2 at 20 mg/l, which can be explained by its high adsorption capacity and the formation of a stable protective layer on the metal surface. Gossypol resin-based compositions, on the other hand, were effective at higher concentrations. The system prepared in diesel solvent shows slightly higher results compared to the kerosene solvent variant (*e.g.*, 90% and 88% in H_2S+CO_2 at 200 mg/l, respectively). In general, the highest efficiency for all inhibitors is observed in the H_2S+CO_2 mixed medium. A comparative graphical dependence of the effectiveness of Marza-3 and Gossypol resin on concentration is presented in Figure 4.

The graphical results more clearly confirm the regularities observed in the table. For all inhibitor systems, the inhibitor efficiency increases monotonically as the concentration increases, and this increase is especially sharp in the H_2S+CO_2 environment.

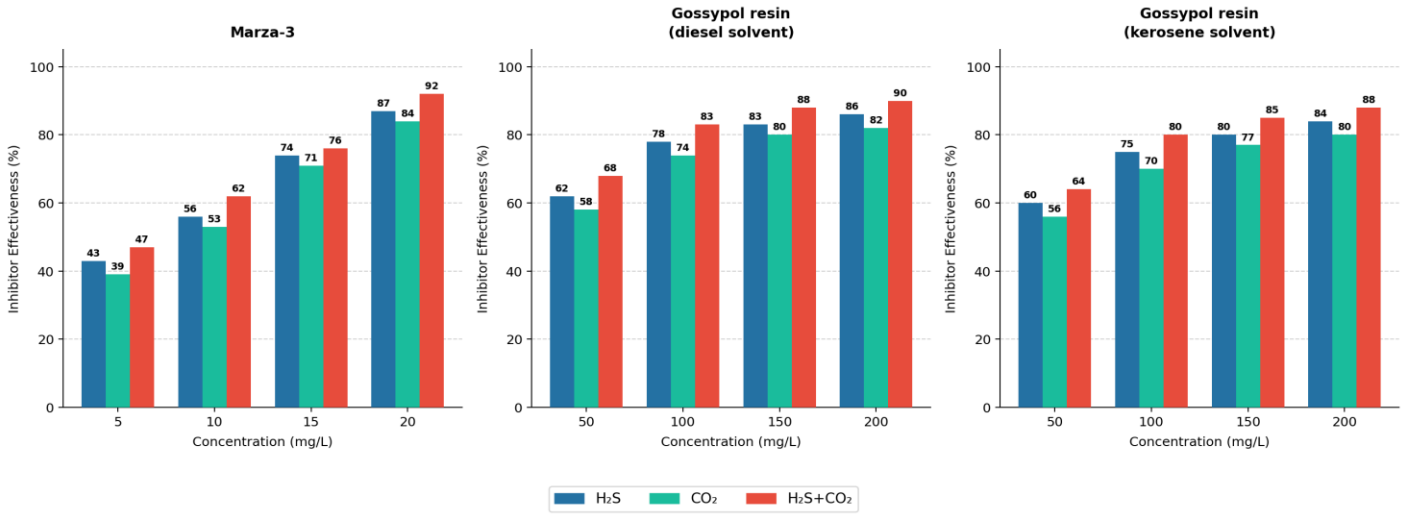


Figure 4. Concentration dependence of the effectiveness of Marza-3 and Gossypol resin in different media.

3.2. Bactericidal properties

3.2.1. Bactericidal effect of Marza-3 and Gossypol resin in SRB medium (S%)

The bactericidal effect of Marza-3 and Gossypol resin against sulfate-reducing bacteria was studied in a comprehensive manner. In the studies, *Desulfovibrio desulfuricans* and *Desulfomicrobium* bacterial species characteristic of the oil industry were selected, the experiments were carried out in Postgate medium for 7 days and the experimental results are reflected in Table 4–6 and Figure 5–7.

The change in the bactericidal effect of Marza-3 against SRB by days is presented in Table 4.

Table 4. Bactericidal effect of Marza inhibitor against SRB.

Bacterial environment	*C* (mg/l)	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
D. desulfuricans	5	2	20	28	35	40	45	50
	10	10	30	66	77	80	83	84
	15	20	46	76	82	83	85	86
	20	40	60	80	84	85	86	87
Desulfomicrobium	5	0	14	32	38	44	48	50
	10	6	22	50	62	68	72	74
	15	14	36	62	74	78	80	80
	20	30	50	77	84	86	88	89

As can be seen from Table 4, Marza-3 has a bactericidal effect against both bacterial species, and this effect increases with both time and concentration. In particular, for *D. desulfuricans*, the level of S≈80% was reached already on the 3rd day at a concentration of 20 mg/l, indicating that the inhibitor has a rapid mechanism of action. Although a similar trend was observed for *Desulfomicrobium*, in some cases the bacteria seemed to be more resistant. The observed bactericidal effect can be explained by the fact that the inhibitor molecules damage the bacterial cell membrane and weaken metabolic activity.

A comparative graphical dependence of the bactericidal effect of the Marza-3 inhibitor on concentration is shown in Figure 5.

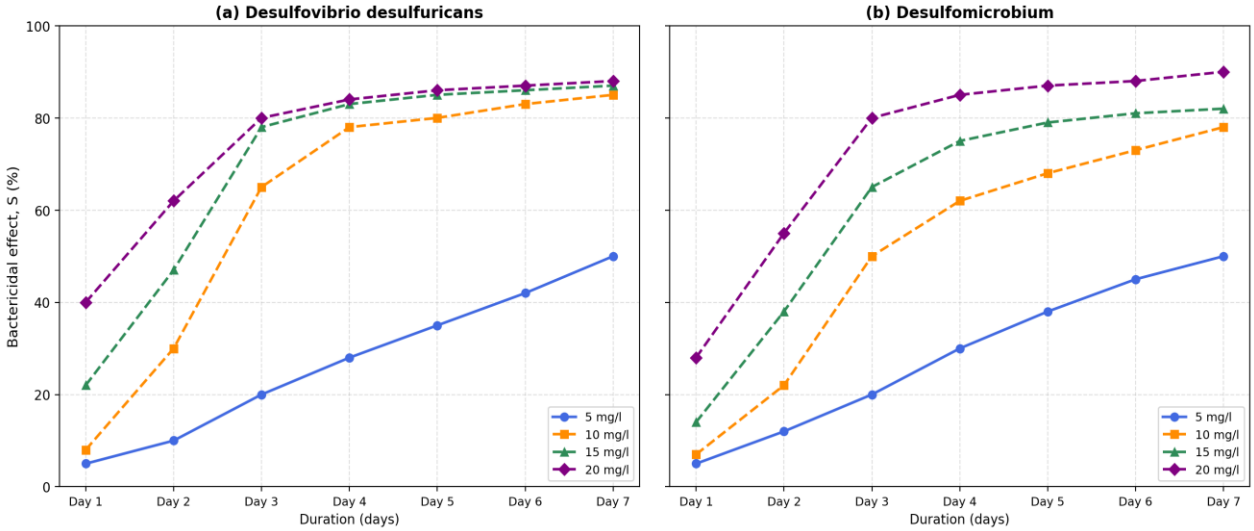


Figure 5. Concentration dependence of the bactericidal effect of Marza-3.

The dependences presented in Figure 5 show that the bactericidal effect has a non-linear growth character and approaches the saturation stage after a certain concentration interval. This is due to the fact that the active centers reach the maximum saturation level especially at high concentrations.

The time-dependent change in the bactericidal effect of gossypol resin against SRB in diesel solvent is presented in Table 5.

Table 5. Bactericidal effect of gossypol resin (diesel solvent) against SRB.

Bacterial environment	*C* (mg/l)	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
D. desulfuricans	50	2	18	25	32	37	44	47
	100	8	27	47	52	58	63	72
	150	18	43	56	58	61	65	74
	200	34	48	62	65	66	67	76

Bacterial environment	*C* (mg/l)	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
Desulfomicrobium	50	3	21	43	52	59	64	73
	100	11	29	49	55	62	66	75
	150	20	46	59	59	64	69	77
	200	36	50	64	67	69	72	79

The results of Table 5 show that Gossypol resin exhibits a moderate to high level of bactericidal effect in diesel media. The maximum effect is observed at a concentration of 200 mg/l and reaches S≈79% in *Desulfomicrobium* bacteria by day 7.

A comparative graph of the bactericidal effect of gossypol resin (diesel solvent) on concentration is shown in Figure 6.

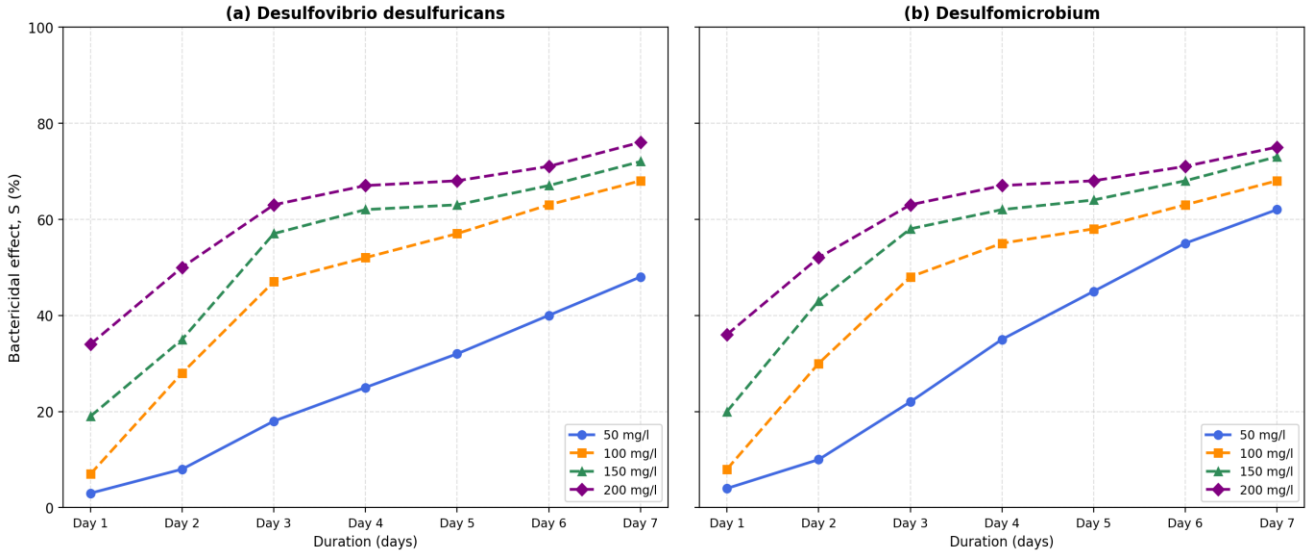


Figure 6. Concentration dependence of the bactericidal effect of gossypol resin (diesel solvent).

As can be seen from Figure 6, although the increase in bactericidal effect is proportional to the concentration, the growth rate decreases at high concentrations.

The results of the bactericidal effect of gossypol resin against SRB in kerosene solvent are given in Table 6.

Table 6. Bactericidal effect of gossypol resin (kerosene solvent) against SRB.

Bacterial environment	*C* (mg/l)	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
D. desulfuricans	50	1	10	20	26	32	37	45
	100	5	16	24	30	43	45	49
	150	12	22	28	35	46	49	56
	200	21	30	33	49	54	57	70
Desulfomicrobium	50	3	12	21	30	35	42	48
	100	9	23	27	34	37	46	54
	150	18	27	30	37	45	50	63
	200	26	34	35	41	48	55	72

Table 6 shows that the bactericidal effect of Gossypol resin in kerosene is relatively weak compared to diesel. Although the maximum effect is achieved at a concentration of 200 mg/l, the overall level remains lower.

A comparative graph of the bactericidal effect of Gossypol resin (kerosene solvent) on concentration is presented in Figure 7.

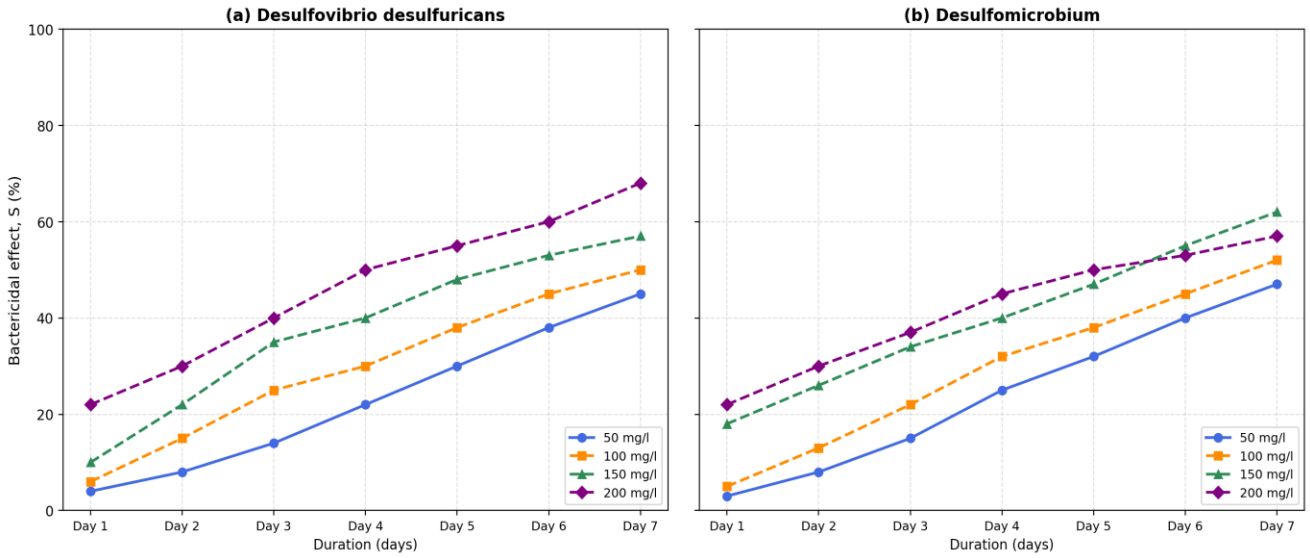


Figure 7. Concentration dependence of the bactericidal effect of gossypol resin (kerosene solvent).

The results in Figure 7 confirm that the bactericidal effect in the kerosene medium shows a weaker growth trend. Although the effect increases with increasing concentration, the saturation stage occurs earlier.

In order to more clearly assess the effect of inhibitors on the metabolic activity of SRB, the amount of biogenic H_2S was determined by iodometric titration depending on the concentration of the inhibitor and the results are presented in Table 7. At the same time, a suitable graphical dependence for visual analysis of this dependence is given in Figure 8. The analysis was carried out for the 7th day, at which stage the effect of the inhibitor in the system is formed at the maximum level. The amount of biogenic H_2S in the reagent-free medium was 134 mg\l.

Table 7. Dependence of the decrease in the amount of biogenic H_2S on the concentration of the inhibitor on the 7th day.

***C* (mg/l)**	***D. desulfuricans***	***Desulfomicrobium***
Marza-3		
5	85.0	85.0
10	27.2	44.2
15	23.8	34.0
20	22.1	18.7
Gossypol resin – in diesel solvent		
50	90.1	45.9
100	47.6	42.5
150	44.2	39.1
200	40.8	35.7
Gossypol resin – in kerosene solvent		
50	93.5	88.4
100	86.7	78.2
150	74.8	62.9
200	51.0	47.6

Figure 8 shows the variation of biogenic H_2S as a function of inhibitor concentration for day 7. While the H_2S content in the reagent-free medium was 134 mg/l, all inhibitor systems significantly reduced this indicator. Gossypol resin showed a higher inhibition effect in the diesel medium, reducing the H_2S content more significantly.

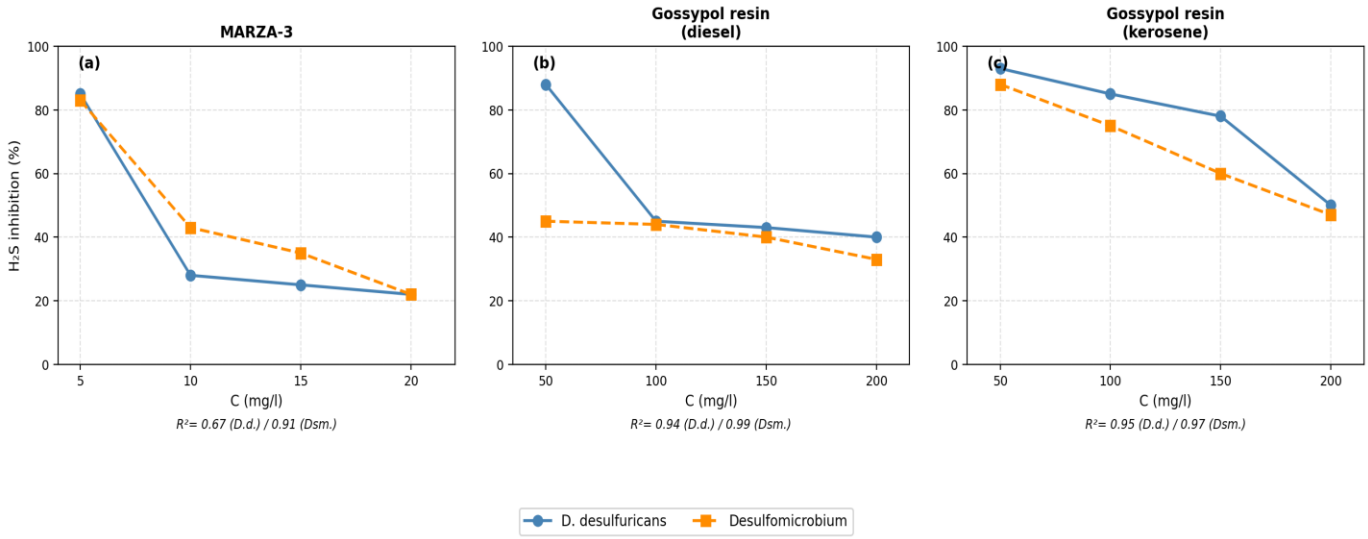


Figure 8. Dependence of the amount of biogenic H_2S on the concentration of the inhibitor on day 7.

3.3. Anti-corrosion effectiveness of new compositions

The comparative graphical dependence of the anti-corrosion effect of the prepared Composition-1: (Gossypol resin (in diesel fuel) + Marza-3) and Composition-2: (Gossypol resin (in kerosene solvent) + Marza-3) evaluated by the gravimetric method in various aggressive environments (H_2S, CO_2 and H_2S+CO_2) and at various concentrations is presented in Figure 9.

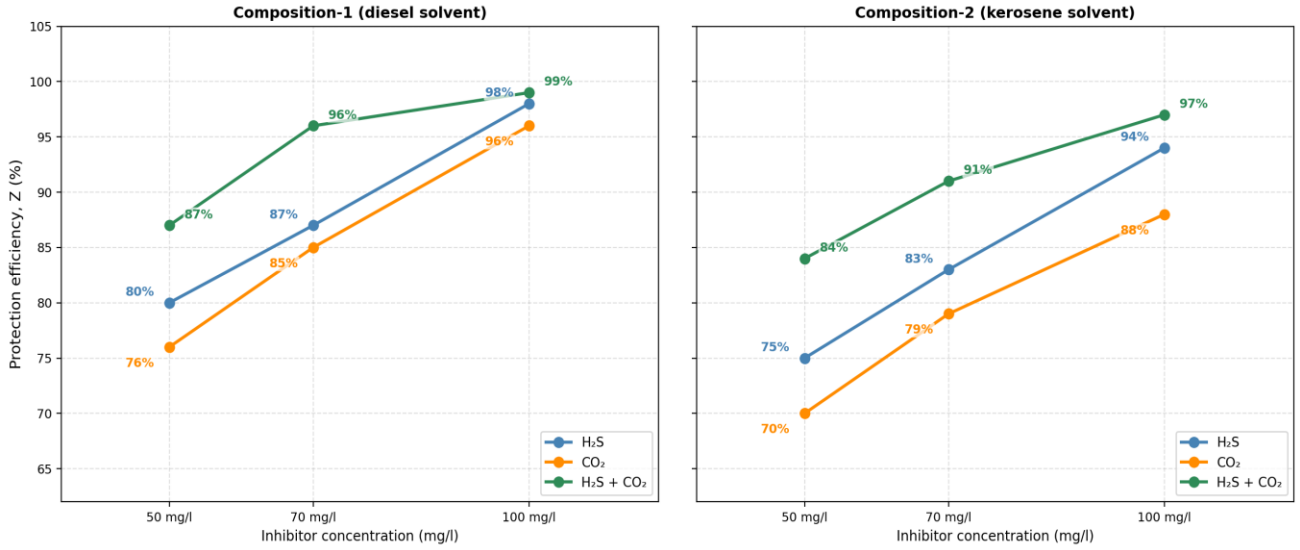


Figure 9. Dependence of the protective effect of the compositions on the concentration.

As can be seen from the figure, Composition-1 shows a slightly higher efficiency than Composition-2 and its maximum protective effect in H_2S+CO_2 environment reaches approximately 99%.

3.4. Bactericidal properties of new compositions

The bactericidal effect of both compositions against SRB at concentrations of 50, 70, 100 and 120 mg/l was determined by tests conducted in Postgate medium for 7 days. The results obtained are reflected in the following Tables 8 and 9 and in Figures 10–12.

Table 8. Bactericidal effect of Composition-1 against SRB.

Bacterial environment	*C* (mg/l)	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
D. desulfuricans	50	10	28	58	68	76	83	86
	70	18	38	66	74	79	86	90
	100	28	54	72	80	85	90	92
	120	48	68	80	84	89	94	98
Desulfomicrobium	50	8	22	28	36	44	54	61
	70	14	30	37	42	49	62	70
	100	22	36	41	49	55	67	79
	120	30	40	46	53	62	78	95

Table 8 shows that Composition-1 exhibits high bactericidal activity and this effect increases sharply with increasing concentration. In particular, for *D. desulfuricans*, S≈98% was reached on day 7 at a concentration of 120 mg/l, indicating almost complete bacterial inactivation.

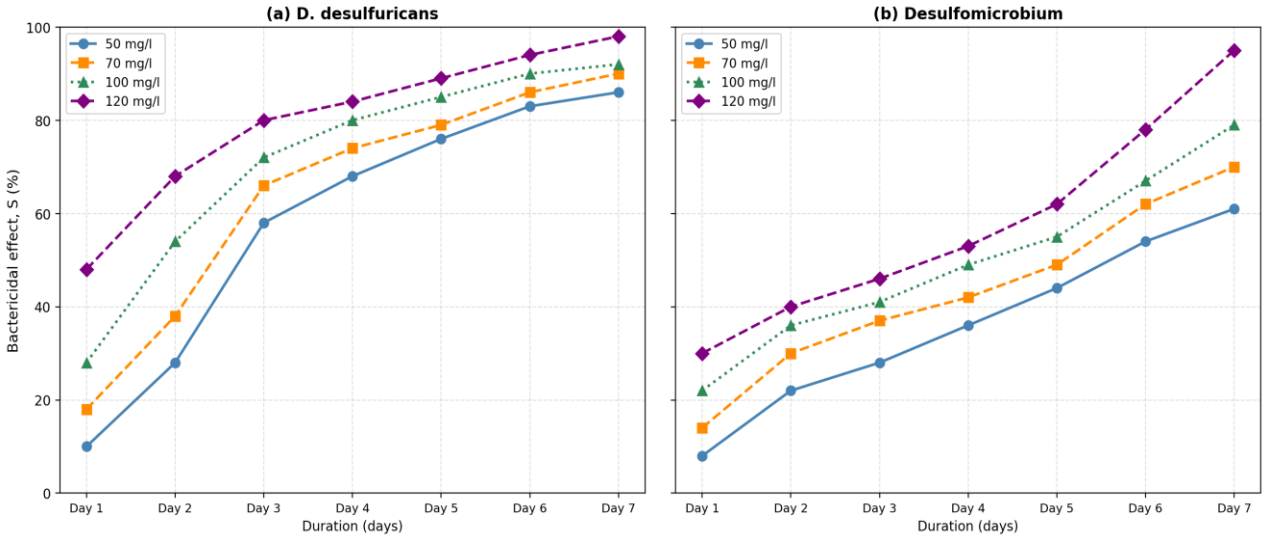


Figure 10. Concentration dependence of the bactericidal effect of Composition-1.

As can be seen from Figure 10, the increase in the bactericidal effect is nonlinear and approaches a maximum at high concentrations. This is explained by the adsorption of active components on the cell surface and the saturation of the action centers.

The dependence of the mass loss of steel samples on the concentration of Composition-1 in the SRB medium is shown in Figure 11.

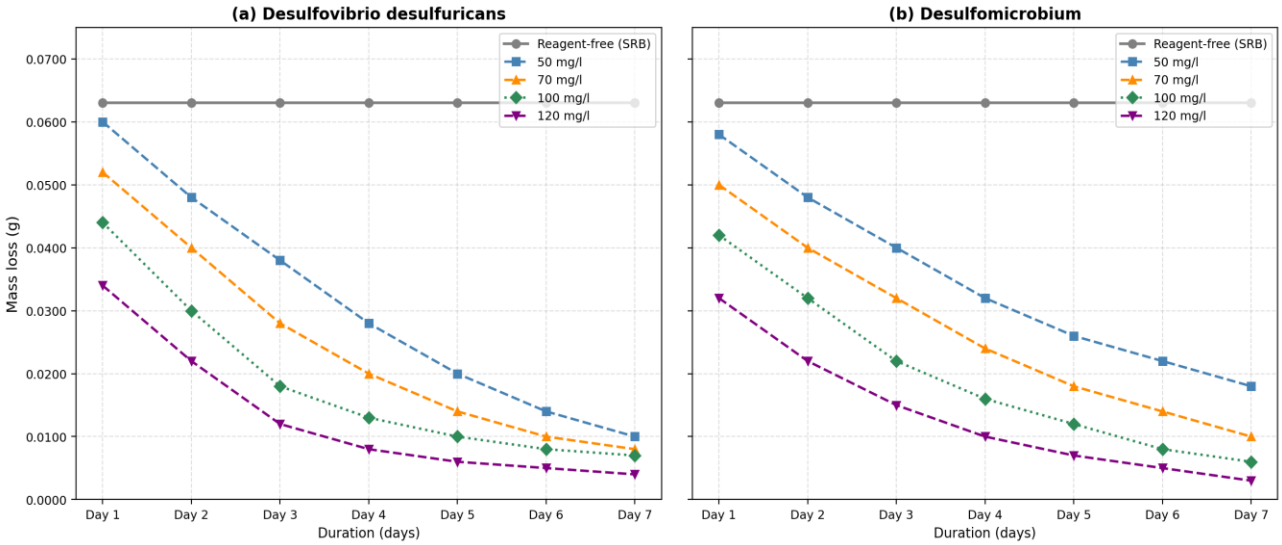


Figure 11. Effect of Composition-1 concentration on the mass loss of steel samples in the SRB medium.

As can be seen from Figure 11, the mass loss of steel samples decreases with increasing inhibitor concentration. This trend indicates that higher concentrations of the inhibitor enhance the formation of a protective film on the metal surface, effectively limiting the access of aggressive species and suppressing corrosion processes in the SRB medium.

Table 9. Bactericidal effect of Composition-2 against SRB.

Bacterial environment	*C* (mg/l)	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
D. desulfuricans	50	8	20	32	43	52	63	72
	70	15	30	38	49	60	69	84
	100	24	36	45	56	67	77	90
	120	32	44	54	68	74	84	96
Desulfomicrobium	50	6	18	29	36	48	52	66
	70	11	24	31	40	52	58	76
	100	18	30	38	45	58	67	83
	120	23	35	42	50	64	75	93

As can be seen from Table 9, Composition-2 also shows high bactericidal activity, but the overall efficacy is slightly lower than that of Composition-1. The maximum effect is achieved at a concentration of 120 mg/l and high *S* values are observed for the 7th day.

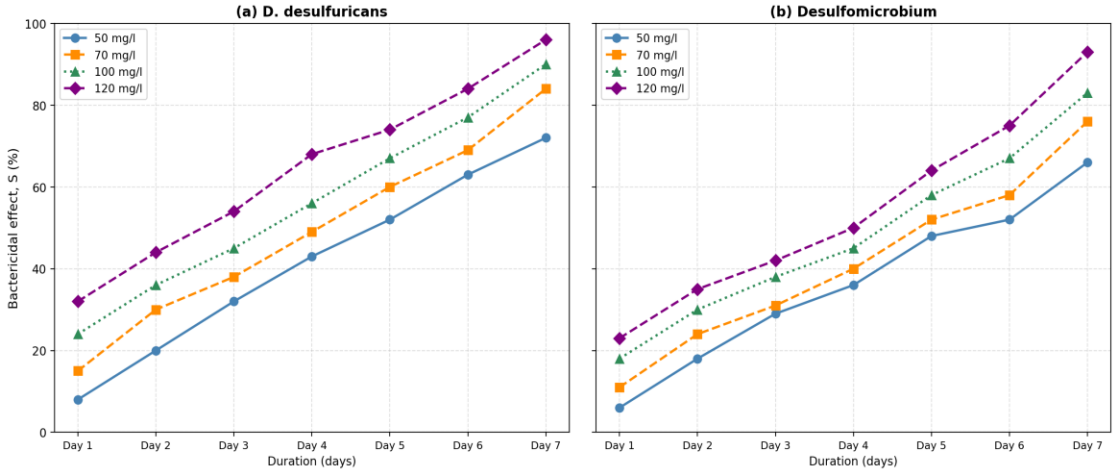


Figure 12. Concentration dependence of the bactericidal effect of Composition-2.

As shown in Figure 12, the bactericidal effect of Composition-2 increases with concentration. However, when compared to Composition-1, the rate of increase is lower. This behavior can be attributed to the relatively lower bioavailability of the active components in the kerosene medium.

Overall, the results indicate that both compositions exhibit significant bactericidal activity against SRB. However, Composition-1 demonstrates superior performance, achieving higher inhibition levels at comparable concentrations.

Figure 13 shows the effect of Composition-1 concentration on the corrosion rate of steel samples in the SRB medium.

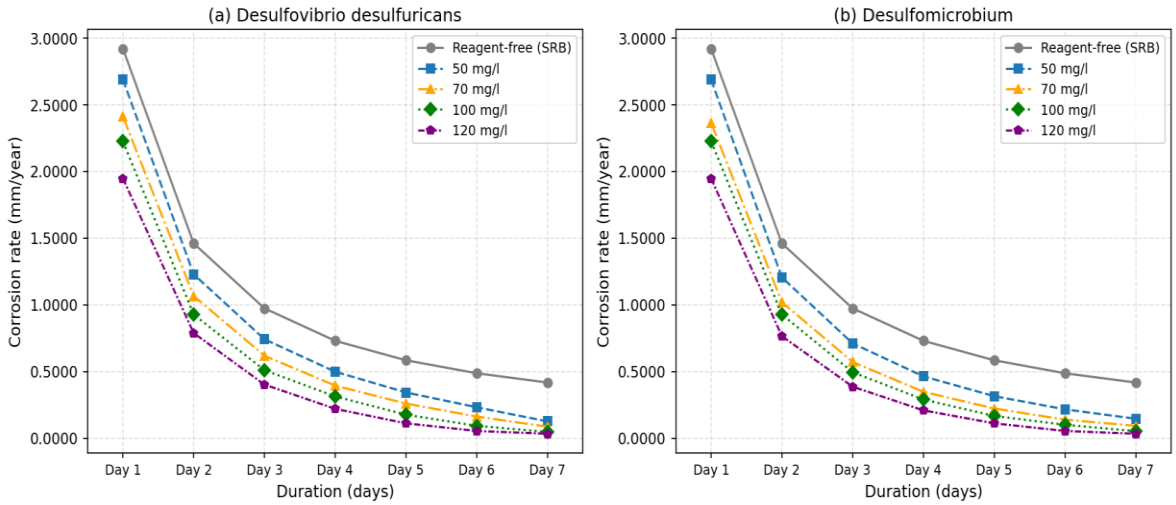


Figure 13. Effect of Composition-1 concentration on the corrosion rate of St-3 steel in the SRB medium.

Figure 13 shows that the corrosion rate decreases with increasing inhibitor concentration, confirming the formation of a protective film on the metal surface. This behavior indicates effective adsorption of the inhibitor molecules and the development of a stable protective layer under SRB conditions.

Thus, the results obtained show that both compositions exhibit bactericidal activity against SRB, with Composition-1 demonstrating superior performance.

The results of the conducted experimental studies show that the compositions prepared on the basis of Gossypol resin and Marza-3 act as a multifunctional protective system with high efficiency in multicomponent corrosion environments. Based on the results of gravimetric tests, it was determined that the effectiveness of corrosion protection during their combination, compared to the individual application of the components, increases significantly and reaches a maximum value at the ratio of Marza-3: Gossypol resin = 1:1. This result clearly confirms the existence of a synergistic interaction between the components. The high efficiency of the combined system is probably explained by the joint action of two different adsorption mechanisms. The nitrogen and oxygen heteroatoms in the Marza-3 molecule form coordination bonds with the active centers of the metal surface, providing mainly chemical adsorption. The phenolic and aromatic structures of the gossypol resin create a physical adsorption and hydrophobic barrier effect through π-electron systems. As a result of the combination of these two mechanisms, a more compact and stabilized protective layer is formed on the metal surface, limiting the diffusion of aggressive ions. In the SRB environment without inhibitors, deep pitting corrosion foci, roughening, biofilm residues and accumulation of FeS-type corrosion products were observed on the metal surface. One of the important results of the study is the high effectiveness of the inhibitor system against microbiological corrosion. It was determined that the compositions significantly weaken the development of sulfate-reducing bacteria and sharply reduce the formation of biogenic hydrogen sulfide. The high correlation (R^2=0.947) between the corrosion protection efficiency and the amount of biogenic H_2S indicates that the intensity of corrosion processes is directly related to microbiological activity. Comparative analysis showed that the diesel-based composition exhibits a higher protective and bactericidal effect compared to the kerosene-based system. This is due to better dispersion of active components in the diesel medium and more effective adsorption on the metal surface. However, the kerosene-based system can be considered more suitable for application at low temperatures.

3.5. Schematic explanation of the inhibition mechanism

The mechanism of action of the new compositions is complex and is explained by the combined effect of several parallel processes. At the first stage, inhibitor molecules are adsorbed on the metal surface, forming a compact and stable protective layer. This layer limits the diffusion of aggressive components (H_2S, CO_2 and Cl^- ions) to the metal surface, thereby reducing the rate of electrochemical corrosion processes. At the same time, the components of the inhibitor weaken the adsorption of sulfate-reducing bacteria to the surface

and their formation in the biofilm. As a result, bacterial metabolism is inhibited and the formation of biogenic hydrogen sulfide is significantly reduced. Thus, as a result of the formation of an adsorption barrier and the combined effect of the bactericidal effect, both electrochemical and microbiological corrosion processes are inhibited in parallel, and the overall corrosion rate is significantly reduced. Thus, the inhibition mechanism is associated with the formation of a protective layer on the metal surface and the reduction of microbiological activity in the SRB medium, which together contribute to the decrease in corrosion rate. This behavior is consistent with literature reports on similar systems.

It should be noted that the experiments in this study were carried out at a constant temperature of 298 K. The primary objective of the work was to evaluate the synergistic effect and multifunctional behavior of the inhibitor system under controlled laboratory conditions. The effect of temperature on corrosion processes and inhibitor performance is well known. In general, an increase in temperature leads to an acceleration of corrosion reactions and may reduce the efficiency of inhibitors due to desorption of inhibitor molecules from the metal surface. However, in some cases, especially for chemically adsorbed inhibitor systems, the efficiency may remain stable or even improve at elevated temperatures. Considering the presence of heteroatoms and π-electron systems in the structure of Marza-3 and phenolic groups in gossypol resin, it can be assumed that the inhibitor system may exhibit relatively stable performance at moderately elevated temperatures due to strong adsorption interactions. A detailed investigation of temperature effects will be the subject of future studies.

Conclusion

As a result of the conducted studies, the properties of the combined inhibitor system based on Marza-3 and plant-based Gossypol resin in multi-component corrosion environments were comprehensively evaluated. It was found that the protective effectiveness of the inhibitor depends not only on the concentration factor, but also on the synergistic effect between the components of the system. In particular, compositions prepared in a 1:1 ratio effectively weaken the effect of the aggressive environment by forming a more compact and durable protective layer on the metal surface. Comparative analyses showed that the type of solvent used significantly affects the performance characteristics of the inhibitor, and diesel-based systems demonstrate higher protective capabilities. In addition, the effect of the inhibitor system is not limited to the inhibition of electrochemical corrosion, but also affects microbiological corrosion processes by reducing the activity of sulfate-reducing bacteria. The results obtained show that the presented compositions, in addition to forming an effective protective barrier on the metal surface in aggressive environments rich in H_2S and CO_2, comprehensively weaken the main causes of corrosion by reducing the formation of biogenic hydrogen sulfide. This approach can be evaluated as a more efficient and universal protection strategy for multicomponent systems. Thus, the developed inhibitor system can be offered as both an environmentally safer and functionally superior alternative for long-term protection of equipment used in the oil and gas industry.

Acknowledgements

The authors would like to thank the "Corrosion Protection" laboratory of the SOCAR "Oil and Gas Scientific Research" Institute for their support of the research.

Author Contributions

Huseyn R. Gurbanov, Saida M. Pashayeva, Gulahmed M. Talibov and Ismayil Ozdemir: conceptualization, implementation of experimental work and preparation of the manuscript. Zang Y. Xin and N. Shirinova: drafting, editing and conclusion of the manuscript.

Funding

This study was conducted without any external research, and the authors received their own funds.

Data Availability

The results of this study are freely available.

Conflict of Interest

The authors declare that they have no identifiable financial or personal interests in connection with this study.

References

1. E.A. Flores, O. Olivares, N.V. Likhanova, M.A. Domínguez-Aguilar, N. Nava, D. Guzman-Lucero and M. Corrales, Sodium phthalamates as corrosion inhibitors for carbon steel in aqueous hydrochloric acid solution, *Corros. Sci*., 2011, **53**, 3899–3913. doi: 10.1016/j.corsci.2011.07.023
2. A. Dehghani, F. Poshtiban, G. Bahlakeh and B. Ramezanzadeh, Fabrication of metal-organic based complex film based on three-valent samarium ions-[bis (phosphonomethyl) amino] methylphosphonic acid (ATMP) for effective corrosion inhibition of mild steel in simulated seawater, *Constr. Build. Mater*., 2020, **239**, 117812. doi: 10.1016/j.conbuildmat.2019.117812
3. B. Lin and Y. Zuo, Corrosion inhibition of carboxylate inhibitors with different alkylene chain lengths on carbon steel in an alkaline solution, *RSC Adv*., 2019, **9**, 7065–7077. doi: 10.1039/C8RA10083G
4. K.S. Bokati, C. Dehghanian and S. Yari, Corrosion inhibition of copper, mild steel and galvanically coupled copper-mild steel in artificial sea water in presence of 1H-benzotriazole, sodium molybdate and sodium phosphate, *Corros. Sci*., 2017, **126**, 272–285. doi: 10.1016/j.corsci.2017.07.009

5. G. Khan, W.J. Basirun, S.N. Kazi, P. Ahmed, L. Magaji, S.M. Ahmed, G.M. Khan, M.A. Rehman and A.B.B.M. Badry, Electrochemical investigation on the corrosion inhibition of mild steel by Quinazoline Schiff base compounds in hydrochloric acid solution, *J. Colloid Interface Sci*., 2017, **502**, 134–145. doi: 10.1016/j.jcis.2017.04.061
6. M. Finšgar and J. Jackson, Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: A review, *Corros. Sci*., 2014, **86**, 17–41. doi: 10.1016/j.corsci.2014.04.044
7. I.B. Onyeachu, M.M. Solomon, S.A. Umoren, I.B. Obot and A.A. Sorour, Corrosion inhibition effect of a benzimidazole derivative on heat exchanger tubing materials during acid cleaning of multistage flash desalination plants, *Desalination*, 2020, **479**, 114283. doi: 10.1016/j.desal.2019.114283
8. S.A. Umoren, M.M. Solomon, I.B. Obot and R.K. Suleiman, A critical review on the recent studies on plant biomaterials as corrosion inhibitors for industrial metals, *J. Ind. Eng. Chem*., 2019, **76**, 91–115. doi: 10.1016/j.jiec.2019.03.057
9. C. Verma, L.O. Olasunkanmi, E.E. Ebenso and M.A. Quraishi, Substituents effect on corrosion inhibition performance of organic compounds in aggressive ionic solutions: A review, *J. Mol. Liq*., 2018, **251**, 100–118. doi: 10.1016/j.molliq.2017.12.055
10. N. M'hiri, D. Veys-Renaux, E. Rocca, I. Ioannou, N.M. Boudhrioua and M. Ghoul, Corrosion inhibition of carbon steel in acidic medium by orange peel extract and its main antioxidant compounds, *Corros. Sci*., 2016, **102**, 55–62. doi: 10.1016/j.corsci.2015.09.017
11. A. Ostovari, S.M. Hoseinieh, M. Peikari, S.R. Shadizadeh and S.J. Hashemi, Corrosion inhibition of mild steel in 1 M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawsone, Gallic acid, α-D-Glucose and Tannic acid), *Corros. Sci*., 2009, **51**, 1935–1949. doi: 10.1016/j.corsci.2009.05.024
12. M. Behpour, S.M. Ghoreishi, M. Khayatkashani and N. Soltani, Green approach to corrosion inhibition of mild steel in two acidic solutions by the extract of *Punica granatum* peel and main constituents, *Mater. Chem. Phys*., 2012, **131**, 621–633. doi: 10.1016/j.matchemphys.2011.10.027
13. S. Garai, S. Garai, P. Jaisankar, J.K. Singh and A. Elango, A comprehensive study on crude methanolic extract of *Artemisia pallens* (Asteraceae) and its active component as effective corrosion inhibitors of mild steel in acid solution, *Corros. Sci*., 2012, **60**, 193–204. doi: 10.1016/j.corsci.2012.03.036
14. M. Faiz, A. Zahari, K. Awang and H. Hussin, Corrosion inhibition on mild steel in 1 M HCl solution by Cryptocarya nigra extracts and three of its constituents (alkaloids), *RSC Adv*., 2020, **10**, 6547–6562. doi: 10.1039/C9RA05654H
15. M. Faustin, A. Maciuk, P. Salvin, C. Roos and M. Lebrini, Corrosion inhibition of C38 steel by alkaloids extract of *Geissospermum laeve* in 1 M hydrochloric acid: Electrochemical and phytochemical studies, *Corros. Sci*., 2015, **92**, 287–300. doi: 10.1016/j.corsci.2014.12.005

16. P. Mourya, S. Banerjee and M.M. Singh, Corrosion inhibition of mild steel in acidic solution by *Tagetes erecta* (Marigold flower) extract as a green inhibitor, *Corros. Sci*., 2014, **85**, 352–363. doi: 10.1016/j.corsci.2014.04.036
17. X. Zhang, Y. Guo, L. Guo, H. Jiang and Q. Ji, In vitro evaluation of antioxidant and antimicrobial activities of *Melaleuca alternifolia* essential oil, *BioMed Res. Int*., 2018, 2396109. doi: 10.1155/2018/2396109
18. S. Shapira, S. Pleban, D. Kazanov, P. Tirosh and N. Arber, Terpinen-4-ol: A novel and promising therapeutic agent for human gastrointestinal cancers, *PLoS ONE*, 2016, **11**, e0156540. doi: 10.1371/journal.pone.0156540
19. N. Pazyar, R. Yaghoobi, N. Bagherani and A. Kazerouni, A review of applications of tea tree oil in dermatology, *Int. J. Dermatol*, 2013, **52**, 784–790.
20. J.Y. Kim, I. Shin and J.W. Byeon, Corrosion inhibition of mild steel and 304 stainless steel in 1 M hydrochloric acid solution by tea tree extract and its main constituents, *Materials*, 2021, **14**, 5016. doi: 10.3390/ma14175016
21. G. Gurbanov, M. Adygozelova, G. Talybov and X. Zhang, Study of the effectiveness of the new inhibitor in different aggressive media, *Nafta-Gaz*, 2023, **7**, 478–483. doi: 10.18668/NG.2023.07.05
22. G. Gurbanov and S. Pashayeva, The inhibitory effect of selected reagents on karbon steel corrosion in formation water containing hydrogen sulfide, *Nafta-Gaz*, 2024, **1**, 55–60. doi: 10.18668/NG.2024.01.07
23. G. Gurbanov and A. Gasimzade, Enhancing demulsification efficiency and corrosion protection in oil industry: a study of novel compositions, *Voprosy Khimii i Khimicheskoi Tekhnologii*, 2024, **2**, 18–25. doi: 10.32434/0321-4095-2024-153-2-18-25 (in Russian).
24. S. Pashayeva, Comparative study of the effect of gossypol resin and HS-1 inhibitors on the corrosion rate in aggressive corrosion environments, *Nafta-Gaz*, 2025, **2**, 128–132. doi: 10.18668/NG.2025.02.05

♦ ♦ ♦