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Original Article

Experimental and Theoretical Studies of *Salsola oppositifolia* Extract as a Novel Eco-Friendly Corrosion Inhibitor for Carbon Steel in 3% NaCl

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Abstract *- This study used an extract from Salsola oppositifolia as an environmentally friendly and sustainable corrosion inhibitor for St20 carbon steel in a 3% NaCl solution. The experimental findings were corroborated through computational methods. The corrosion-inhibiting properties of the extract were evaluated using weight loss measurements and electrochemical potentiodynamic polarization, alongside surface analysis conducted via SEM (Scanning Electron Microscopy) and AFM (Atomic Force Microscopy). The weight loss measurements and electrochemical experiments demonstrated that the Salsola oppositifolia extract acted as an effective corrosion inhibitor. The efficiency of corrosion inhibition increased with higher concentrations of the plant extract, exceeding 93.82% at concentrations of 400, 600, and 1000 mg* L^{-1}. *This notable inhibitory performance was attributed to the extract's strong adsorption onto the steel surface and its mixed-type behaviour, with adsorption data fitting well into the Langmuir isothermal model. Further investigations at an optimal concentration and immersion time of 240 hours indicated the stability of the adsorbed inhibitor layer on the St20 surface in 3% NaCl media.*

Keywords *- Salsola oppositifolia, Green corrosion inhibitor, Langmuir isotherm, Weight loss measurements, Electrochemical potentiodynamic polarization, SEM, AFM.*

1. Introduction

Metals can be protected against corrosion in different corrosive environments using corrosion inhibitors, which are compounds added in small quantities to a corrosive solution to reduce or minimize the corrosion rate[1, 2]. The economic impact of corrosion is substantial; for instance, according to international research by NACE (IMPACT 2016), the annual global economic damage due to corrosion amounts to approximately 2.5 trillion US dollars[3, 4].

This represents about 3.4% of the average Gross Domestic Product (GDP) of each country[5]. In recent years, there has been growing interest in environmentally friendly corrosion protection methods to reduce pollution from waste and toxins. Green inhibitors, such as plant extracts, are not only environmentally friendly but also more cost-effective than chemically synthesized inhibitors[6].

Various plant parts, including leaves, stems, fruits, roots, and seeds, have been used as green inhibitors. For example, Salvia officinalis extract demonstrated 96% efficiency at 2500 mg/L[7], Osmanthus fragrans extract showed 94% suppression efficiency at 340 mg/L[8]., Musa paradisiaca extract achieved 90% suppression efficiency at 300 mg/L[9]. and mangrove tannins trees reached 89% at 6000 mg/L[10].

Other examples include Jasminum nudiflorum extract at 92% efficiency at 1000 mg/L[11], Lawsonia inermis extract at 92% efficiency at 1200 mg/L[12], Dendrocalamus brandisii extract at 90% efficiency at 1000 mg/L[13], Kola nitida extract at 78% efficiency at 1200 mg/L[14], and Murraya koenigii extract at 96% inhibitory efficacy at 600 mg/L[15].

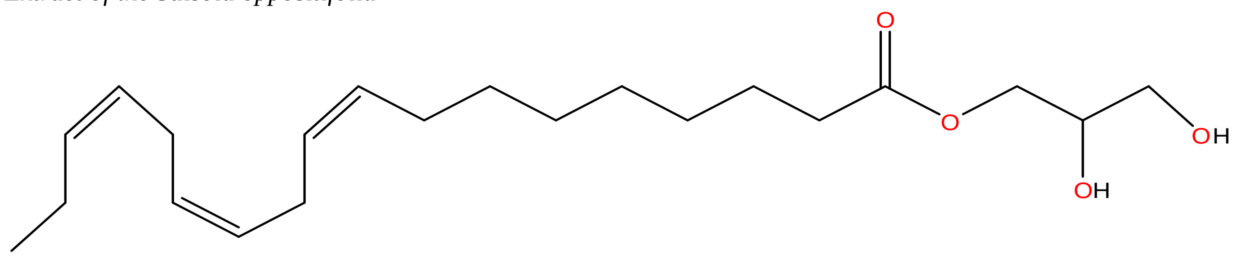
Studies have shown that plants are composed of complex organic compounds: tannins, alkaloids, amino acids, proteins and flavonoids. In turn, such substances contain different polar functional groups and bonds. *Salsola oppositifolia* plant extract is used in medicine as a drug for such diseases as antitumor, hypotensive, diuretic, emollient, laxative, antiulcer, and anti-inflammatory[15-20].

2. Experimental Part

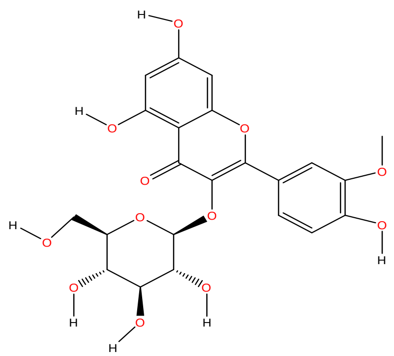
2.1. Materials

The experiments were carried out with samples of carbon steel grade St30, and steel samples of this brand were purchased from "Uzbekistan Metallurgical Combinat" JSC. Corrosion tests and electrochemical and capacitive measurements were carried out on samples of steel St2 with composition, wt. %: C - 0.2; Mn -0.5; Si - 0.15; P-0.04; S - 0.05; Cr -0.30; Ni - 0.20; Cu - 0.20; Fe - 98.36. A sample of size (1.21 cm^2) was taken, and its mass loss was examined gravimetrically. These specimens were sanded with 100, 200, 500, 1000 and 1500 grade sandpaper, rinsed and degreased with acetone and distilled water prior to testing. The experiment was tested using 3 % NaCl media.

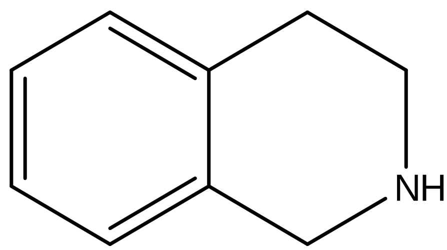
2.1.1. Extract of the Salsola oppositifolia



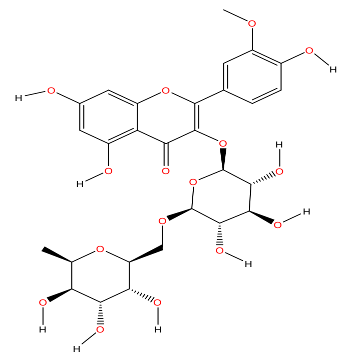
Linolenic acid, 2-hydroxy-1(hydroxymethyl) ethyl ester



Isorhamnetin-3-O-glucoside



Tetrahydrozoxinoline



Isorhamnetin 3-O-rutinosides

Fig. 1 The main molecules of extracts of the *Salsola oppositifolia*

2.2. Methods

2.2.1. Polarization Curves Analysis

The corrosion-inhibiting properties of an aqueous dispersion of the studied corrosion inhibitor *Salsola oppositifolia* extract, both with and without additives, were studied by the potentiostatic method on a CS-350(Figure 2). Corrosion test, by recording polarization curves on steel electrodes in corrosion media 3% NaCl saline media. Ag/AgCl was used as the reference electrode. Platinum was used as the counter electrode. For the experiment, only 1.2 cm^2 of each electrode was immersed in the corrosive environment. Each electrode was placed parallel to the other at a distance of 1 cm, and the Ag/AgCl electrode was placed between the other two electrodes. These three types of electrodes were tested without inhibitors and in solutions with different concentrations of inhibitors. The measurements were made using a sine wave with an amplitude of 10 mV at a frequency from 10 kHz to 0.01 Hz at an open-circuit electronic potential. Polarization curves were performed from -160 mV to +160 mV at a scan rate of 1 mV s^{-1}. The electrochemical initial input range was 2.5 V, with a maximum potential resolution of 760 mV and a potential accuracy of 300 mV with an apparatus containing a noise module. The data recorded by this device was edited and summarized using the "Origin Lab" program.

Fig. 2 CS-350 cossion test device

2.2.2. SEM and AFM Analysis

Surface morphology and microstructure studies of the samples were carried out using a scanning electron microscope SEM - EVO MA 10 (Carl Zeiss, made in Germany) and AFM - Agilent 5500 (Agilent, USA).

2.2.3. Weight Loss Measurements

A steel sample of size (1.21 cm^2) was used for a practical experiment based on mass loss. Practical experiments were carried out in a solution of *Salsola oppositifolia* extract at various concentrations with the addition of 3 % NaCl saline solution and at different temperatures. The following equations determined corrosion rate (1) and efficiency (2).

$$C_R = \frac{W_b - W_a}{At} \quad (1)$$

$$\eta(\%) = \frac{C_{R(blank)} - C_{R(inhibitor)}}{C_{R(blank)}} \quad (2)$$

Where: $C_{R(blank)}$-corrosion rate, W_b is the metal sample weight until the experiment, W_a is the weight of the metal sample after the experiment, A is the surface area of the sample taken, and t is the time spent on the practical experiment hour. $C_{R(blank)}$- corrosion rate without inhibitor, $C_{R(inhibitor)}$ - corrosion rate with inhibitor.

3. Results and Discussion

3.1. Weight Loss Measurements

The gravimetric method is one of the widely used and effective methods for determining the corrosion rate of metal in laboratory conditions. In this case, the tested metal is determined based on the difference in mass loss in the state where the inhibitor is added to the solution and when it is not added. We also conducted practical experiments to determine the corrosion rate of steel at different temperatures and concentrations, from 400 mg/l to 1000 mg/l.

The inhibitor efficiency (Z%) and corrosion rate of *Salsola oppositifolia* extract at different temperatures and concentrations were determined. It is known from the results that mass inhibitor efficiency increases with the increase of inhibitor concentration (Table 1).

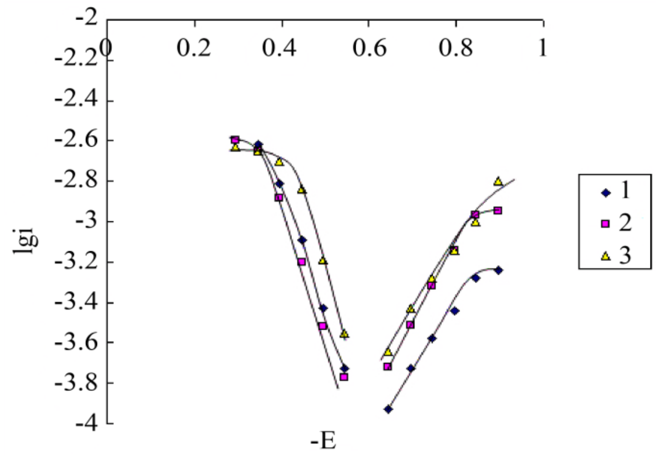
The maximum inhibition efficiency of the green corrosion inhibitor in a 3% NaCl medium was 93.82% at a concentration of 1000 mg/l and a temperature of 333 K.

3.2. Electrochemical Research

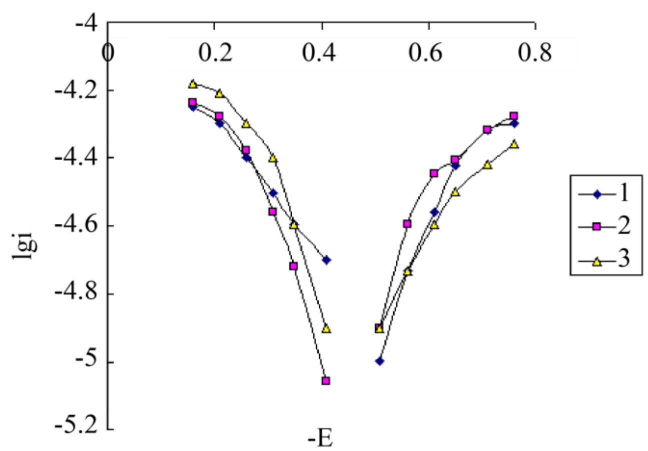
Electrochemical studies have shown that in the presence of the inhibitors we tested, the polarizability of steel sharply increases. Inhibited with green corrosion inhibitors not only participate in the inhibition of the anodic reaction but also significantly affect the cathodic process, creating a barrier to the diffusion of oxidizing agents and aggressive components to the steel.

Table 1. The values of inhibition coefficient (γ), Total surface coverage (θ), Protection level (Z) of 3% NaCl saline *Salsola oppositifolia* extract green inhibitor at different temperatures for 240 hours

Inhibitor	T, (K)	C, (mg/l)	*K*, gr/ (sm^2·soat)	γ	Z, (%)	θ
Green inhibitor	**293**	-	**1.27**	-	-	-
		400	0,264	4,81	79,15	0,7915
		600	0,226	5,62	82,21	0,8221
		1000	0,131	10,69	93.82	0, 9382



Inhibitor concentration mg/l, 1-400; 2-600; 3-1000.
Fig. 3 Polarization curves of the *Salsola oppositifolia* extract green inhibitor in 3% NaCl saline solution



Inhibitor concentration mg/l, 1-400; 2-600; 3-1000.
Fig. 4 Electrochemical Polarization Behavior of *Salsola Oppositifolia* Extract in 3% NaCl Solution

Thus, when exposed to aggressive environments, corrosion lesions appear on control samples within the first day and on inhibited samples after 10–12 days. The aftereffect and potential of steel, as can be seen from the data presented, depend on the time of exposure to inhibitors. In Table 2, the corrosion current value of the solution with and without green corrosion inhibitor decreased from 0.98±0.11 i,(mA/cm2) to 0.067±0.001 i,(mA/cm2). The efficiency of green corrosion inhibitors in 3% NaCl saline solution showed an improvement in corrosion inhibitors. As can be seen from the data given in Table 3, the value of the corrosion current of the 3% (NaCl) saline solution was 0.884±0.12 *i*, (mA/cm^2). As the concentration of the green corrosion inhibitor in the solution increases, the electric resistance of the solution also increases. As a result, the potential amount of the corrosion current value also decreases, and the corrosion current value decreases to 0.077±0.01*i* (mA/cm^2). When the concentration of the green corrosion inhibitor was 1000 mg/l, the efficiency was 91.23% in 3% (NaCl) saline media.

Table 2.Weight loss data for St20 steel in 3% NaCl saline solution without and with different concentrations of *Salsola oppositifolia* extract for 4 h at 298 K

Inhibitor	C, (mg/l)	*i*, (mA/sm^2)	γ	θ	η, (%)
Blank	-	0,98±0,11	–	–	–
Salsola oppositifolia extract	400	0,21±0,08	4,67	78,29	0,7829
	600	0,15±0,05	6,53	84,46	0,8446
	1000	0,067±0.001	13,19	93,17	0,9317

Table 3. Weight loss data for St20 steel in 3% NaCl saline solution without and with different concentrations of *Salsola oppositifolia* extract for 6 h at 298 K

Inhibitor	C, (mg/l)	*i*, (*m*A/sm^2)	γ	θ	η, (%)
Blank	-	0,884±0,12	–	–	–
Salsola oppositifolia extract	400	0,174±0.07	5,08	0,8026	80,26
	600	0,148±0,05	5,97	0,8325	83,25
	1000	0,077±0.01	11,48	0,9123	91,23

3.3. Adsorption Isotherms

The process of adsorption is the desorption of water molecules by adsorbing inhibitor molecules on the metal surface, and this process can also be described as an exchange process. From this, we can see that the inhibitor is adsorbed on the metal surface and covers the surface (θ).

As the inhibitor concentration increases, the surface is covered to a higher degree and the efficiency increases. θ is a quantity indicating the effectiveness of the inhibitor and is taken as 100. Several types of isotherms have been used to describe this process. Freundlich adsorption isotherms were obtained, which can be expressed as follows:

$$\theta = K_{ads}C^n \quad (3)$$

or

$$log\theta = logK_{ads} + nlogC \quad (4)$$

Where 0<n<1; θ–surface coating; C-inhibitor concentration; Kads-Equilibrium constant of cads-adsorption-desorption process.

The following isotherms for the adsorption of these corrosion inhibitors were also studied.

$$\text{Lengmiur:} \frac{C_{\text{ing}}}{\theta} = \frac{1}{K_{ads}} + C_{\text{ing}} \quad (5)$$

$$\text{Frumkin:} \quad \frac{\theta_{grav}}{1-\theta_{grav}} exp(-2f\theta_{grav}) = K_{ads}C_{ing} \quad (6)$$

$$\text{Tyomkin:} \quad exp(f\theta_{grav}) = K_{ads}C_{ing} \quad (7)$$

Where C_{inh} is the concentration of the inhibitor in the solution (mg/l), θ-full coverage, K_{ads}-adsorption equilibrium constant.

The standard free energy of adsorption ($\Delta G°_{ads}$) is calculated by the following equation (8).

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

Here, R is the universal gas constant, T is the absolute temperature in Kelvin, and ρ_W is the density of water in g/l. The values of k_{ads} and $\Delta G°_{ads}$ are calculated using the above isotherm equations.

A negative value of $\Delta G°_{ads}$ indicates that the adsorption has reached a high peak. The value of $\Delta G°_{ads}$ showed a range of -40.5 kJ mol^{-1} and -43 kJ mol^{-1} for the Langmuir adsorption isotherm. The value of $\Delta G°_{ads}$ for the Tyomkin isotherm is between -32 kJ mol^{-1} and -40 kJ mol^{-1}. The value of $\Delta G°_{ads}$ -40 kJ mol^{-1} is the equilibrium state of chemical and physical adsorption. If the value of $\Delta G°_{ads}$ is up to -20 kJ mol^{-1}, it is considered to represent physisorption, and if the value of $\Delta G°_{ads}$ is more negative than -40 kJ mol^{-1}, it is considered to represent chemical sorption.

In Figure 5 of green corrosion inhibitor. Tyomkin (Figure 5 a), Frumkin (Figure 5 b), and Langmuir (Figure 5 c) isotherms are also plotted. According to the obtained results, when comparing the values of Frumkin, Tyomkin and Langmuir isotherms, the value of the Langmuir isotherm is higher than 0.99, which shows us that it matches the experimental data for the calculation of thermodynamic parameters.

Langmuir, Frumkin and Tyomkin isotherms for green corrosion inhibitors were also studied. Correlation coefficient values were obtained at different temperatures. In Figures 5a and 5b the values of the correlation coefficients of the Frumkin and Tyomkin adsorption isotherms are not close to 1, indicating that the adsorption process does not proceed according to these isotherms.

The values of K_{ads} were calculated based on the intercept of the Langmuir isotherms. It follows from the values of K_{ads} that the adsorption of green corrosion inhibitor on the metal surface is superior to all desorptions. Based on the data in Table 4, ΔG^0_{ads} values were obtained in the range of 303−333 K, and the results ranged from negative -23.11 kJ/mol to -28.21 kJ/mol, indicating the adsorption of green corrosion inhibitor confirms that it occurs spontaneously on the surface of the metal.

3.4. Atomic Absorption Method

Today, at least some part of the technology of the industry has to work in an aggressive environment. As we all know, metal constructions are corroded in the environment. Based on the method of atomic absorption spectrometry, we can determine the concentration of metal dissolved in the corrosion process. The concentration of iron ions in the solution of *Salsola oppositifolia* extract with and without extract was determined. In this case, the main aggressive environment is water in the cooling system, pH = 8-9.

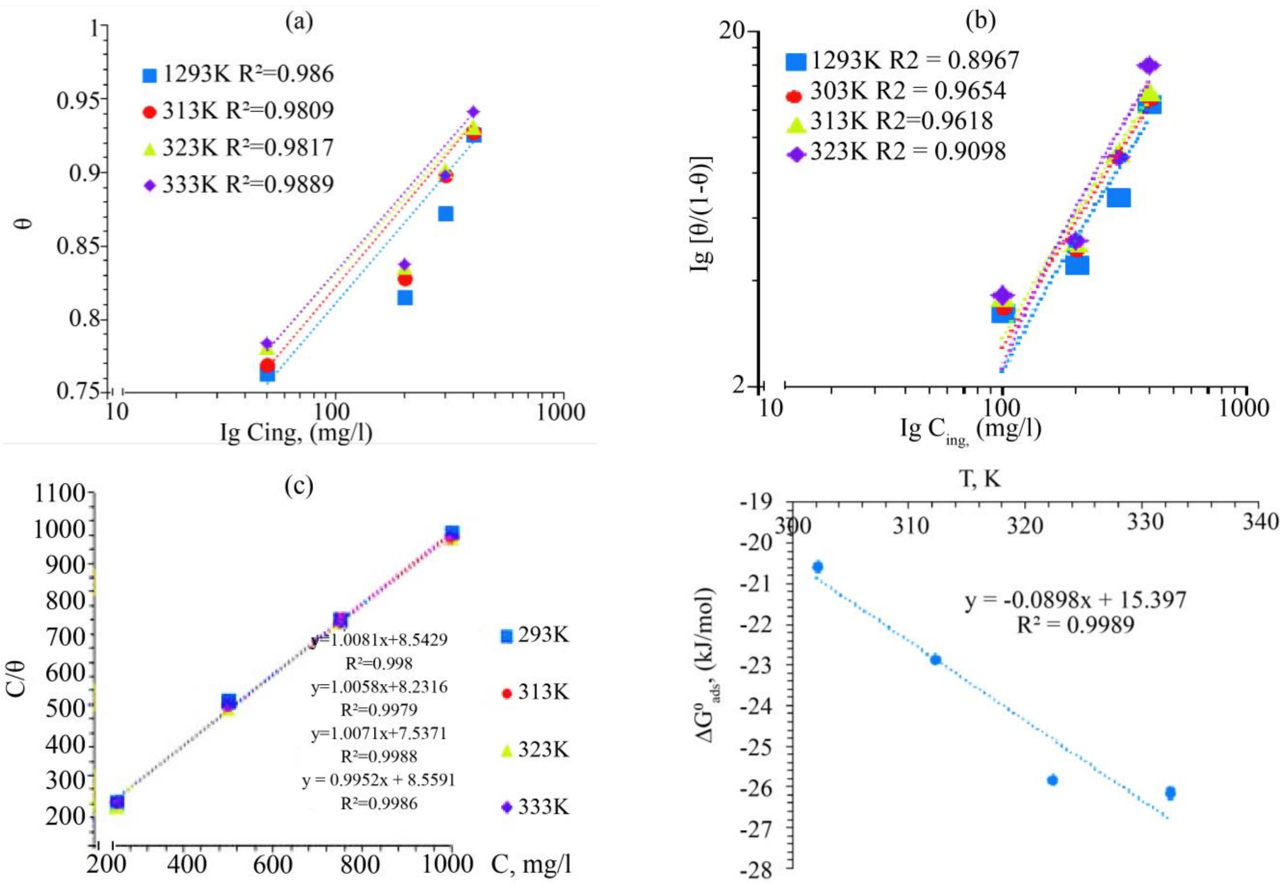


Fig. 5 (a) Tyomkin (b) Frumkin (c) Langmuir isotherms (d) Temperature dependence of ΔG^0_{ads}

Table 4.Thermodynamic parameters of green corrosion inhibitor

Harorat	K_{ads}	ΔG_{ads} kJ/mol	$\Delta H_{ads,}$ (kJ/mol)	$\Delta S_{ads,}$ (kJ/mol K)
303	357,2	-23,11	-15,39	-127,4
313	433,1	-25,32		
323	490,7	-26,41		
333	580,6	-28,21		

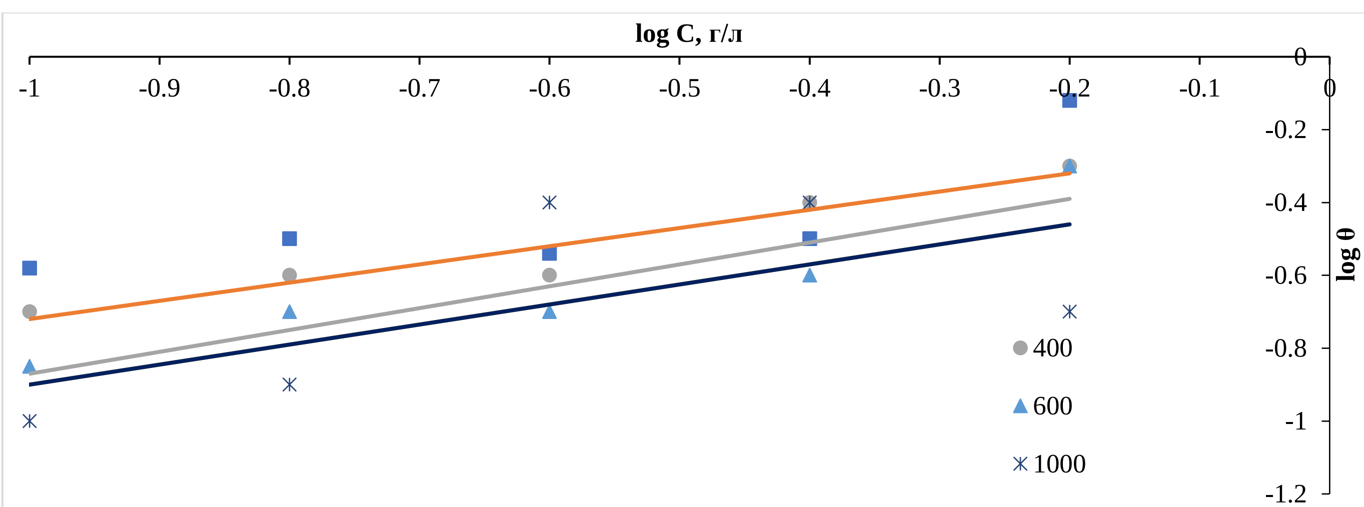


Fig. 6 Freundlich adsorption isotherm for water in the cooling system in the presence of an inhibitor of green corrosion inhibitor at different temperatures

The concentration of steel in the solution without inhibitor was 56 mg/l. In inhibitor solutions, this indicator decreased to 3.78 mg/l. Based on that, we can say that the inhibition efficiency showed the relevant indicators by 93.24%. The indicated inhibition indicators are in good agreement with the indicators determined by other methods.

3.5. SEM and AFM Analysis

The steel surface was examined in three different states: before corrosion, after corrosion, and after corrosion inhibition, using a scanning electron microscope (SEM-EVO MA 10, Zeiss, Germany). Specifically, the morphological characteristics of carbon steel samples at various concentrations were extensively analyzed using SEM imaging techniques. Based on Figure 7, the initial steel sample underwent meticulous cleaning using various grades of sandpaper and was subsequently washed with acetone.

Microphotographs of the untreated steel sample were captured using a scanning electron microscope in an uninhibited environment (Figure 8) and in an inhibited environment (Figure 9).

Figure 10 illustrates the SEM imaging and elemental analysis of corrosion inhibited by the PUA-1 inhibitor brand. The images demonstrate the adsorption of the inhibitor on the steel surface and its protective role against aggressive environments.

In Figure 11, the elemental analysis reveals that the iron content in the annealed steel sample was 87.3%, indicating effective protection by the inhibitor. The scanning was performed at a nano-micro scale, utilizing high-precision instrumentation to study inhibitor effects on corrosion formation and prevention at metal/alloy interfaces[26,27].

Fig. 7 The original photograph of the steel sample

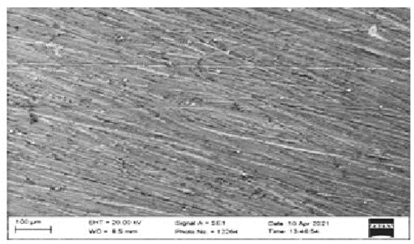


Fig. 8 SEM image of a steel sample

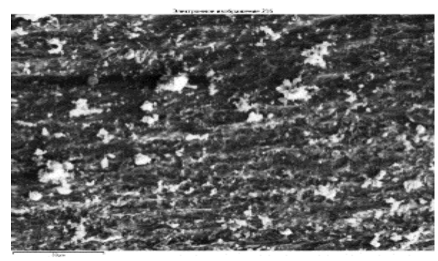


Fig. 9 SEM image of a steel sample after inhibition

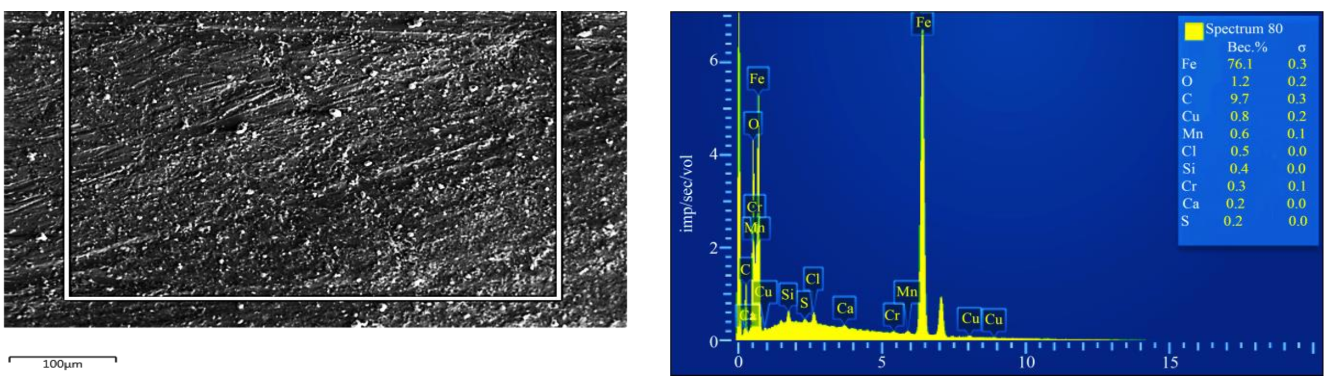


Fig. 10 Scanning Electron Microscopy (SEM) and elemental analysis were conducted on an inhibited St20 steel sample treated with the green inhibitor

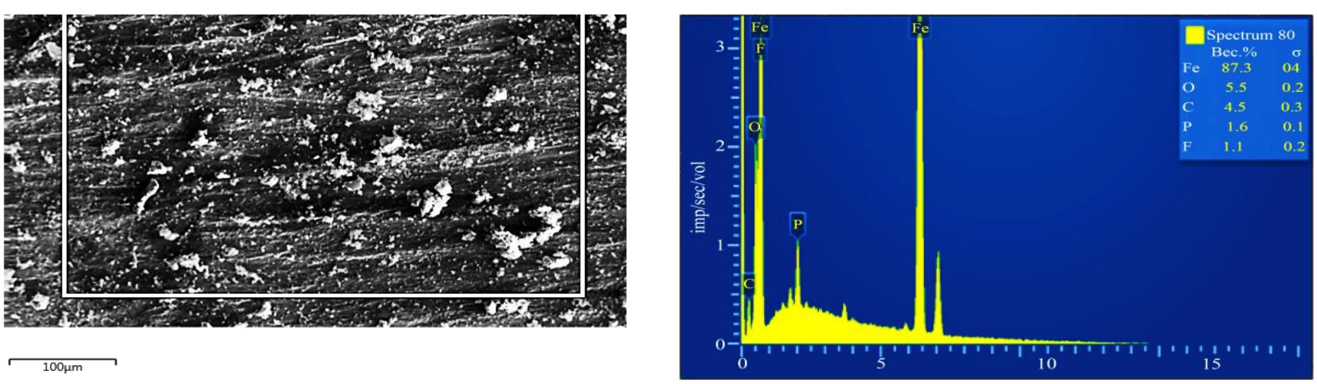


Fig. 11 SEM imaging and elemental analysis were performed on an inhibited St30 steel sample treated with the green inhibitor

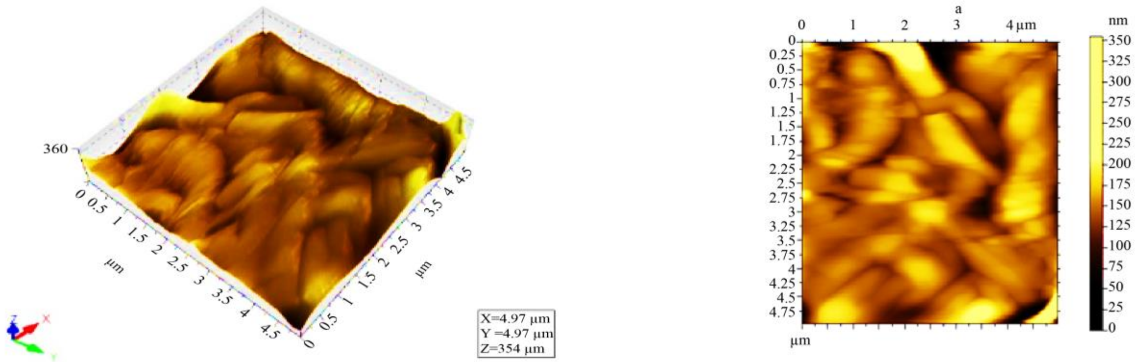


Fig. 12 A photomicrograph displaying the surface morphology of a St20 steel sample in a 3% NaCl saline solution acquired using an Atomic Force Microscope (AFM)

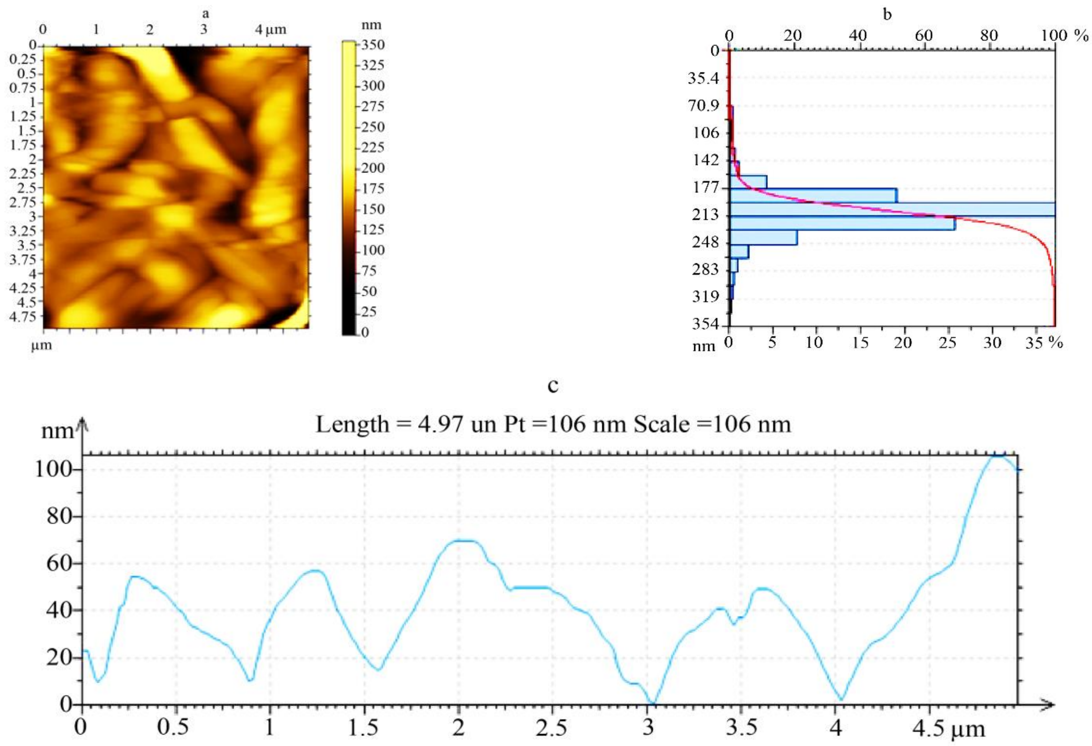


Fig. 13 Topographical analysis of the steel surface

The carbon steel surface was examined at a size of 4.5x4.5 µm, revealing convex peaks measuring approximately 350 nm and depressions measuring 135 nm (Figure 13a). These surface features were visually striking, with wave-like structures reaching a height of 106 nm (Figure 13c). The analysis also identified various concave and convex dimensions on the steel surface, along with areas exhibiting coverage ranging from a minimum of 30% to 100% (Figure 13b) [21-24].

4. Conclusion

According to the obtained results, the extract of the plant *Salsola oppositifolia* was used as a green inhibitor, and its inhibitory efficiency was studied in a 3% NaCl environment. Inhibition efficiency was 93.17% for six hours. It has been determined that the inhibition mechanism obeys the Langmuir isotherm. When the morphology of the inhibited steel surface was studied with the help of a scanning electron microscope and an atomic force microscope, it was found that the green inhibitor was well adsorbed on the steel surface and protected it from the external aggressive corrosion environment.

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Authors' Contribution Statement

Abror Nomozov and Eshkaraev S Ch: Conducted the drafting. Jumaeva Z.E and Todjiev J.N did the conception, design, and drafting; Eshkoraev S.S and Umirqulova F.A participated in the conception, design, and drafting, and all the authors took part in revision and proofreading.

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