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Issue Article

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THE STUDYING OF APPLICATION OF SALSOLA OPPOSITIFOLIA EXTRACT IN 0.5 M L OF SULFURIC ACID AS A GREEN INHIBITOR FOR CORROSION OF CARBON STEEL

***Abstract**: In recent years, we can see that in the protection of metals from corrosion, effective results are obtained using not only corrosion inhibitors synthesized by chemical methods, but also extracts from various parts of plants. In this article, research has been conducted on obtaining an eco-friendly inhibitor and its application in practice. The source of the green inhibitor was the Salsola oppositifolia plant, from which the method of obtaining the green inhibitor extract and extrareagents were studied. The obtained extract was studied as a green inhibitor in 0.5 M* H_2SO_4 *solution for corrosion protection of carbon steel structures. In determining the efficacy of a green inhibitor derived from the salsola oppositifolia plant, practical experiments were performed at two different temperatures (298 K and 313 K) and at different concentrations (200 mg / l, 400 mg / l, 600 mg / l, and 1000 mg / l). Adsorption of Green inhibitor on steel surface was studied using Langmuir and Temkin isotherms.*

The effect of temperature and concentration on the corrosion rate was also studied. The gravimetric method was used to determine the effectiveness of the green inhibitor and it was found that its maximum concentration was 91.86%. The mechanism of action of the Green inhibitor on the steel surface and a post-experimental steel sample were studied by SEM analysis. Salsola oppositifolia plant extract contains a number of flavonoids, iso flavonoids (isorhamnetin-3-O-glucoside and isorhamnetin-3-O-rutinoside), organic acids (Methyl palmitate, palmitic acid, Linoleic acid, linoleic acid). 2-hydroxy-1- (hydroxymethyl) ethyl ester) and tetrahydroisoquinoline.

Salsola oppositifolia extract is a good green inhibitor due to the presence of hetero atomic organic compounds in the main component.

Key words: *Salsola oppositifolia, green inhibitor, Langmuir izotermasi, Temkin isotherm, H_2SO_4.*
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Introduction

It is difficult to imagine our modern world without industry, because many manufacturing enterprises are required to meet the needs of mankind. It is no secret that all types of industrial equipment are made of steel. Such steel structures operate in various acidic conditions, which can seriously damage the stability of steel structures, as well as lead to serious economic losses [1]. At present, inorganic and organic substances are used in many industrial enterprises to prolong the stability of steel structures and increase their economic efficiency, inhibitors are used. It should be noted that many of the synthesized corrosion inhibitors are harmful to the environment, and also that the cost of such inhibitors is high. In recent years, there has been increased interest in environmentally friendly products in order to protect the environment from pollution by waste and toxins. For example, green inhibitors are not only environmentally friendly, but also much cheaper than chemically synthesized inhibitors [2,3]. Most of the known organic inhibitors consist of heteroatomic compounds that retain the elements N, O, S, P and functional groups based on them, such as NH, NH_2, C=O, OH, COOH, and CHO. The electrons in these heteroaomic compounds form a bond with the free d-orbitals of iron atoms on the steel surface based on the electron-donor-acceptor mechanism. As a result, it blocks the activity of the iron atom due to functional groups in the organic heteroatomic molecule and significantly reduces the degree of corrosion [4–6]. The extract of leaves, stems, fruits, roots and seeds of many plants was used as a green inhibitor. For example: Salvia officinalis extract 96% efficiency at 2500mg/L [7], Osmanthus fragran extract at 340mg/L, 94% suppression efficiency [8], Musa paradisiac extract at 300mg/L, 90% suppression efficiency [9], Mangrove tannins trees 89% at 6000 mg/L [10], 92% at 1000 mg/L Jasminum nudiflorum extract [11], 92% at 1200 mg/L Lawsonia inermis extract [12], 90 % at 1000 mg/l, Dendrocalamus brandisii extract [13], Kola nitida extract at 1200 mg/l at 78% [14], Murraya koenigii extract at 600 mg/l showed 96% inhibitory efficacy [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 [16–18]. Salsola oppositifolia plant extract contains a number of flavonoids, isoflavonoids (isoramnetin-3-O-glucoside and isorhamnetin-3-O-rutinoside), organic acids (methyl palmitate, palmitic acid, linoleic acid, linoleic acid-2).-hydroxy-1-(hydroxymethyl) ethyl ester) and tetrahydroisoquinoline [19].

This article was the first to study the use of Salsola oppositifolia extract as a green inhibitor in 0.5 M H_2SO_4 solution.

EXPERIMENTAL PART

Sample preparation. The composition of the steel obtained for practical experiments is as follows: Steel st20 in accordance with GOST 1050-88 steel grade 20 refers to carbon structural alloys [3; c 761-768] and contains the elements shown in Table 1.

Table 1. Chemical composition in% steel 20 GOST 1050–88

Fe	C	Si	Mn	Ni	S	P	Cr	Cu	As
97,755-97,215	0,17-0,24	0,17-0,37	0,35-0,65	till 0,3	till 0,04	till 0,035	till 0,25	till 0,3	till 0,08

In many ways, the performance of the metal depends on the concentration of carbon, since with an increase in its concentration, the hardness and brittleness of the material increase. According to these indicators, grade 20 steel is classified as "quality structural carbon steel". It is used in the machine-building field to create plain bearings, pipes, shafts and many other products.

Corrosion tests, 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 (0,19625 sm^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. For the experiment, it was tested in a 0.5 M solution of H_2SO_4.

Preparation of Salsola oppositifolia extract**.** Annual sprigs of the aerial stem of Salsola oppositifolia are stored and dried in a dark place for 3-5 days. 100 g dry sample is ground to a powder and mixed with 300 ml methanol in a 0.5 liter flat-bottomed flask at 50°C, incubated for 12 hours. The resulting mixture is filtered, the methanol in the filtrate is dried in vacuum at a temperature of 52-53°C. The mass of the remaining dry residue was 5.84 grams.

For practical experiments, solutions with a concentration of 200, 400, 600 and 1000 mg/L were prepared.

Gravimetric method and inhibitor efficiency**.** A steel sample of size (0,19625 sm^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 0.5 M sulfuric acid solution and at different temperatures. Corrosion rate (1) and efficiency (2) were determined by the following equations**.**

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

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

Where: $C_{R(blank)}$-- corrosion rate, W_b- metal sample weight, untill experiment, W_a- the weight of the metal sample after the experiment, A surface area of the sample taken, t- time spent on the practical experiment, hour.

$C_{R(blank)}$- corrosion rate without inhibitor, $C_{R(inhibitor)}$ - corrosion rate with inhibitor.

RESULTS AND ITS DISCUSSION

Weight loss measurements. The inhibitory efficiency (η%) and the corrosion rate of the Salsola oppositifolia extract were determined at different temperatures and different concentrations. The results show that as the concentration of the inhibitor increases, so does the effectiveness of the inhibitor (Table 2).

Table 2. Corrosion rate and effectiveness of the green inhibitor Salsola oppositifolia in 0.5 M H_2SO_4 at various concentrations and temperatures.

Inhibitor concentration mg/l.	Temperature, K	Corrosion rate g/m², days.	Inhibitor efficiency,%
200	298 K	0,003175	71,56
	313K	0,002895	69,36
400	298 K	0,004125	75,46
	313K	0,003765	72,58
600	298 K	0,003117	88,53
	313K	0,002171	83,76
1000	298 K	0,001125	92,38
	313K	0,001156	91,86

As can be seen from Table 2, at a concentration of 200 mg / l and a temperature of 31.3 K, the efficiency of the inhibitor is 69.36%, and at a concentration of 1000 mg / l, 313 K - 91.86%.

The effect of temperature. Studying the effect of temperature on the corrosion rate and the inhibitor efficiency facilitates the calculation of kinetic and thermodynamic parameters for inhibition and adsorption processes. These parameters are useful for interpreting the type of adsorption by the inhibitor. In general, the effectiveness of the inhibitor decreases with increasing temperature. The activation energy (Ea) of this process is found using the Arrhenius equation 3 [20,21].

$$ln_{(\vartheta_{korr})} = B - \frac{E_a}{RT} \quad (3)$$

Here B is a constant depending on the type of metal, R is the universal gas constant, and T is the absolute temperature. The plot of the absolute temperature (1/T) $ln_{(vcorr)}$ gave a straight line slope = E_a/R, from which the activation energies for the corrosion and inhibition process were calculated.

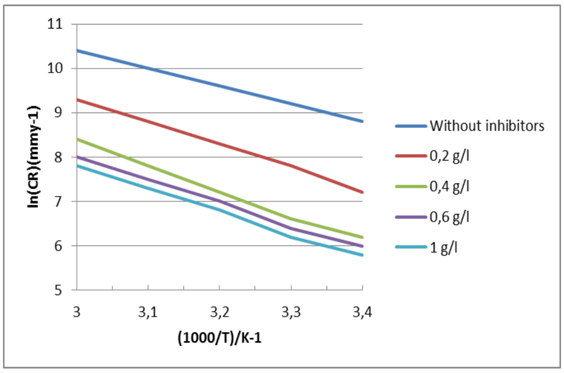


Figure 1. Arrhenius equation for inhibitors of various concentrations for steel in an acidic environment of 0.5 M H_2SO_4.

Using the Arrhenius equation, corrosion at various concentrations was calculated for 0.5 M H_2SO_4 acid with and without inhibitors. Calculated using the transition state equation for the corrosion process using thermodynamic parameters such as enthalpy (ΔH) and entropy (ΔS).

$$\vartheta_{(korr)} = \frac{RT}{Nh}\exp\left(\frac{\Delta S}{R}\right)exp\left(\frac{\Delta H}{RT}\right) \quad (4)$$

Where h is Planck's constant, N - Avogadro's number. have a straight line with an inclination = ΔH/T and intersection 1/T relatively ln (forT) = ln (R / Nh) + ΔS / R.

Dependency plots 1/T от ln(v_{corr}/T) for corrosion of metals show the presence of the inhibitor at various concentrations in Figure 2. The calculated activation parameters are shown in Table 3. If we compare the activation energy (Ea) of the solution used with the inhibitor with the solution used without the inhibitor, we can see that the addition of the inhibitor (Ea) to the solution increases, and the activation energy increases with increasing inhibitor concentration in the solution. High activation energy is physical adsorption, if it does not change or less, then it is chemical adsorption.

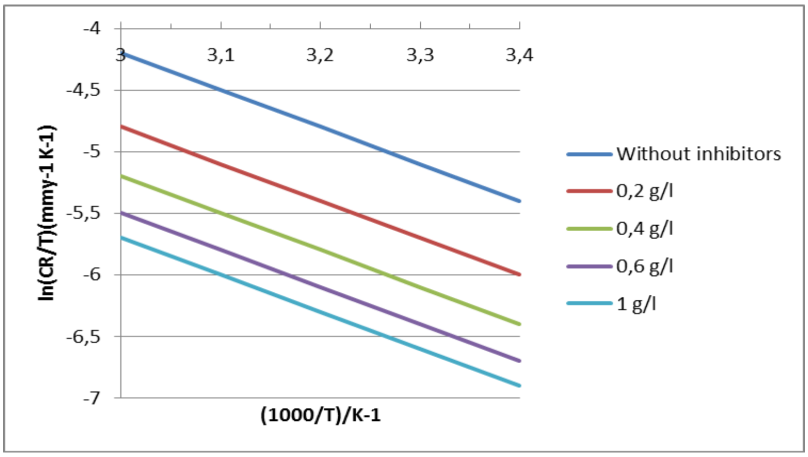


Figure 2. Diagrams 1/T for ln (vcorr/T) corrosion of steel in 0.5 M H_2SO_4 acid containing various inhibitor concentrations.

Table 3. Parameters of activation of 0.5 M acid H_2SO_4 at various inhibitor concentrations.

Inhibitor concentration	E_a (кДжмоль$^{-1}$)	ΔH_a (кДжмоль$^{-1}$)	ΔS_a (кДжмоль$^{-1}$K^{-1})
0.0	42.56	43.74	-101.25
200	58.24	57.86	-75.21
400	63.42	59.93	-52.36
600	75.21	64.14	-23.12
1	88.19	79.63	18.36

As shown in Table 3, the values of activation energy (Ea) increase sharply with increasing inhibitor concentration. Therefore, in preventing corrosion, the main function of an inhibitor is physical desorption on the metal surface. From the large negative entropy values, it can be seen that the phase that determines the corrosion rate. The binding to the formation of the active complex is higher than the dissociation, which leads to a decrease in disorder [22,23].

Adsorption isotherm. The adsorption process refers to the desorption of water molecules by inhibitor molecules adsorbed on the metal surface, as well as the exchange process [24, 25]. 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 also covered to a greater extent and the efficiency increases. (θ) is basically a value indicative of inhibitor efficiency, taken up to 100. The adsorption isotherm was calculated from the Langmuir and Temkin isotherms. The Langmuir adsorption isotherm is represented by the following mathematical equation 5 [26].

$$\frac{C}{\theta} = \frac{1}{k_{ads}} + C \qquad (5)$$

where C is the inhibitor concentration, θ is the degree of surface coverage, and kads is the adsorption equilibrium constant. Mass loss and electrochemical results are measured by the adsorption characteristics of the process. The Temkin isotherm is represented by the equation below (6).

$$\theta = \frac{-lnk_{ads}}{2a} - \frac{lnC}{2a} \qquad (6)$$

In the above equation, the adsorption equilibrium constant kads and the parameters acting on a.

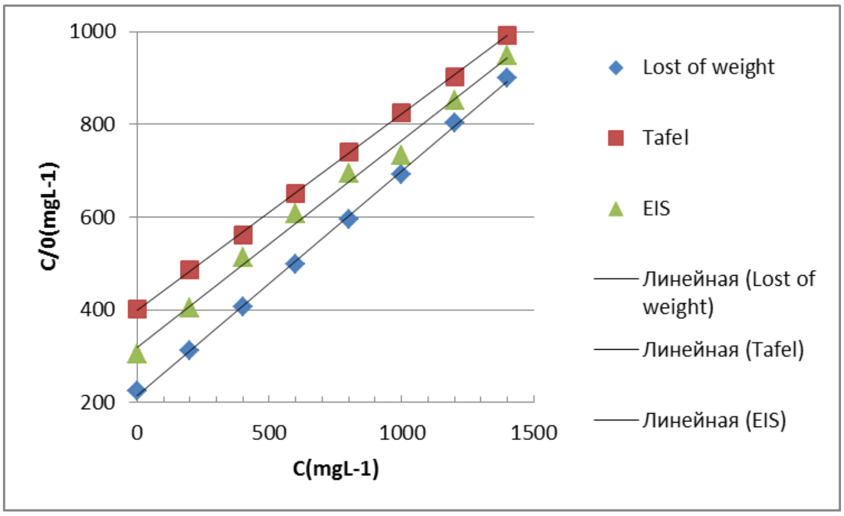


Figure 3. For carbon steel structures in 0.5 M H_2SO_4 acid 1 g/l with and without inhibitors.

Langmuir adsorption isotherm

Standard energy without adsorption (ΔG $°_{ads}$) calculated using formula 7 below.

$$\Delta G^0_{ads} = -RTln(k_{ads} x p_W) \qquad (7)$$

Here R is the universal gas constant, T is the absolute temperature in Kelvin, ρW- density of water in g/l. The values of k_{ads} and $\Delta G°_{ads}$ for Langmuir and Temkin isotherms. The results calculated using Equations 3,4 and 5 above are shown in Table 4.

Table 4. Inhibitory and non-inhibitory parameters of the Langmuir adsorption isotherm for carbon steel in an acidic environment of 0.5 M H_2SO_4 at a concentration of 1 g/l.

Parameters	Mass loss	Tafel	EIS
Langmuir k_{ads}(L g^{-1})	7.42	14.71	17.15
ΔG^0_{ads} (kJmol^{-1})	-43	-40.5	-41.4
lnk_{ads} (L g^{-1})	7	5	5
ΔG^0_{ads} (kJ mol^{-1})	-38	-33	-32

A negative value of ΔG°ads indicates that the adsorption peak has been reached. The ΔG°ads value showed a range from -40.5 kJ mol-1 to -43 kJ mol-1 for the Langmuir adsorption isotherm. The DG °ads value for the Temkin isotherm gives a range of ΔG°ads values from -32 kJ mol-1 to -40 kJ mol-1. The value of ΔG°ads - 40 kJ / mol is the equilibrium state of chemical and physical adsorption. It is assumed that

ΔG°ads represents the physical absorption if the value is less than -20 kJ/mol, and the chemical value if the ΔG°ads value is more negative than 40 kJ/mol.

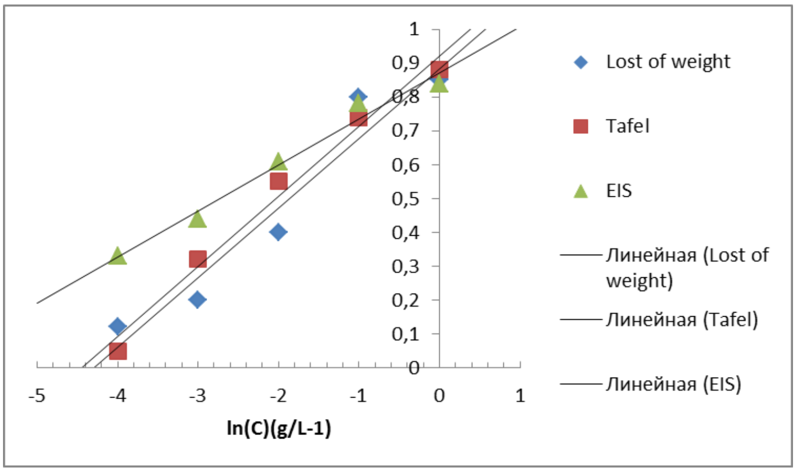
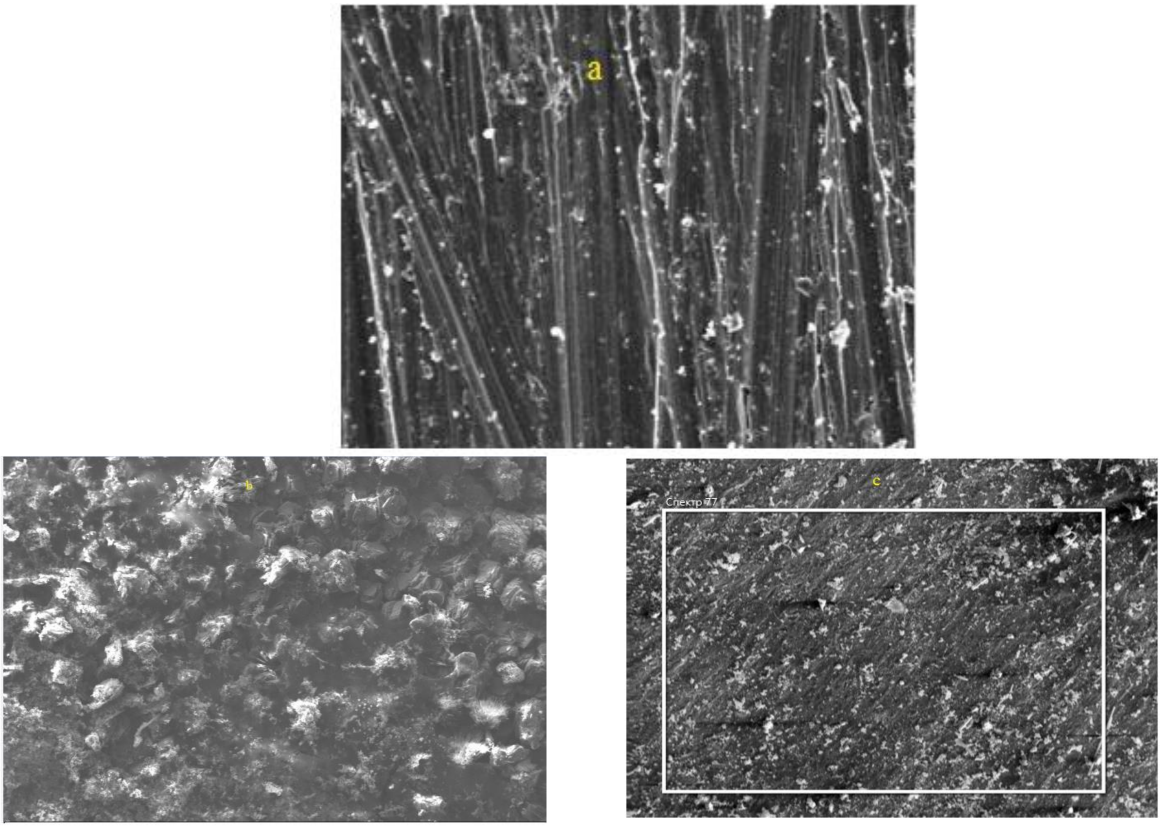


Figure 4. Inhibitor and non-inhibitor parameters of 1 g/L concentration for 0.5 M sulfuric acid medium for carbon steel.



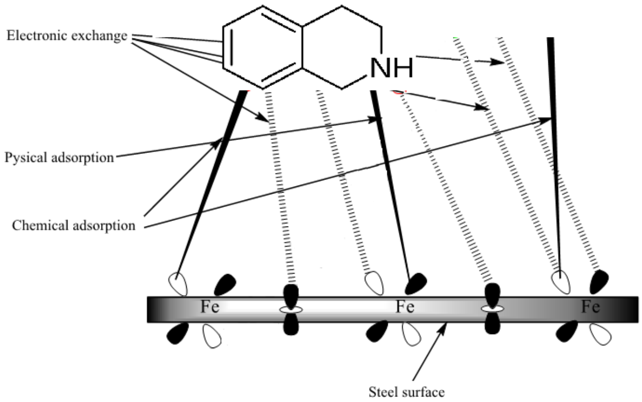
Pic1: SEM images of treated steel [a], steel sample immersed in 0.5 M H_2SO_4 without inhibitors [b], and [c] steel immersed in 0,5 M H_2SO_4 in the presence of Salsola oppositifolia extract.

Scanning electron microscope (SEM). The purpose of this method is to generate various signals on the surface of solid samples using directed beams of high-energy electrons. SEM makes it possible to obtain information from the signals obtained from the electronic interaction of the sample, such as the surface structure (external morphology), chemical composition, component organization, and the crystal structure of the sample. The purpose of SEM analysis is to determine the presence of an inhibitor on the steel surface. In addition, SEM analysis does not lead to a change in the composition of the sample, i.e. does not lead to loss of sample volume during electronic interaction with the sample.

When determining the morphological structure of the metal surface, the samples were examined using a scanning electron microscope. On pic. 1a shows the SEM analysis of the surface of a metal sample before the experiment. Pic.1b shows an example of a steel sample in 0.5 M H_2SO_4 solution without inhibitors after 120 hours. Figure 1c shows a surface view of a 0.5 M H_2SO_4 solution with an extract of Salsola oppositifolia. From the above SEM analysis, the following two mechanisms are known to play a key role in inhibitor adsorption on the steel surface:

a) interaction of the p-electrons of the aromatic rings of the inhibitor with the free d-orbitals of the iron atom on the surface of the steel according to the donor-acceptor mechanism.

b) interaction of undistributed paired electrons in the inhibitor and free d-orbitals of the iron atom on the steel surface according to the donor-acceptor mechanism.



Pic 2: Corrosion protection mechanism

A model of the two mechanisms described above is shown in Pic 1. The figure shows that donor-acceptor interaction with empty d-orbitals on the iron atom of unshared electron pairs in functional groups in heteroatomic organic inhibitors and Vander-Physical and chemical adsorption based on Vander-Waltz forces, play an important role.

CONCLUSION

Based on practical results, it was shown that the extract of the plant Salsola oppositifolia is effective when used as a green inhibitor by 90,86% at a temperature of 313K. The effect of temperature on the process and the results of absorption and isotherm analysis proved that the obtained green inhibitor is not far behind chemically synthesized inhibitors.

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