Salsola Oppositifolia acid extract as a green corrosion inhibitor for carbon steel

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In this article, research has been conducted on obtaining an eco-friendly inhibitor and its application in practice. The source of the green inhibitor is *the Salsola oppositifolia* plant, from which the method of obtaining the green inhibitor extract is studied. The obtained extract is studied as a green inhibitor in 0.5 M HCl solution for corrosion protection of carbon steel structures. In determining the efficacy of a green inhibitor derived from the *Salsola oppositifolia* plant, practical experiments have been 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 has been studied using Langmuir and Temkin isotherms. The effect of temperature and concentration on the corrosion rate is also studied. The gravimetric method is used to determine the effectiveness of the green inhibitor and it is found that its maximum concentration is 91.86%. The mechanism of action of the steel surface and a post-experimental steel sample are studied by scanning electron microscope analysis. *Salsola oppositifolia* extract is a good green inhibitor due to the presence of hetero atomic organic compounds in the main component.

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[1-4]. 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 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[2-6]. 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[6-10]. The extract of leaves, stems, fruits, roots and seeds of many plants was used as a green inhibitor. For example, *Salvia officinalis* extract showed 96% suppression efficiency at 2500 mg/L[11], Osmanthus fragran extract 94% at 340 mg/L[12], Musa paradisiac extract showed 90% at 300 mg/L[13], Mangrove tannins trees showed 89% at 6000 mg/L[14], Jasminum nudiflorum extract[15] showed 92% at 1000 mg/L, Lawsonia inermis extract[16] showed 92% at 1200 mg/L, Dendrocalamus brandisii extract showed 90 % at 1000 mg/L[17], Kola nitida extract showed 78% at 1200 mg/L[18], and Murraya koenigii extract showed 96% inhibitory efficacy at 600 mg/L[19].

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 diseases such as antitumor, hypotensive, diuretic, emollient, laxative, antiulcer, and anti-inflammatory[20–22]. *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[23].

Experimental Section

Materials and methods

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 and contains the elements shown in Table 1.

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 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. For the experiment, it was tested in a 0.5 M solution of HCl.

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 L flat-bottomed flask at 50°C, incubated for 12 h. The resulting mixture was filtered, the methanol in the filtrate was dried in vacuum at a temperature of 52-53°C. The mass of the remaining dry residue was 5.84 g. 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 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 0.5 M hydrochloric acid solution and at different temperatures. Corrosion rate (C_R) and efficiency (η) were determined by the following equations.

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

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

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

Results and Discussion

Weight loss measurement

The inhibitory efficiency *($\eta\%$)* and the corrosion rate of the *Salsola oppositifolia* extract were determined at different temperatures and concentrations. The results show that as the concentration of the inhibitor increases, so does the effectiveness of the inhibitor (Table 2). 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 the efficiency of the inhibitor is 93,87 %.

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 *(E_a)* of this process is found using the Arrhenius equation as in Eq. (3) [24,25].

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

Table 1 — Chemical composition (%) of 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

Table 2 — Parameters of activation of 0.5 M hydrochloric acid at different inhibitor concentrations

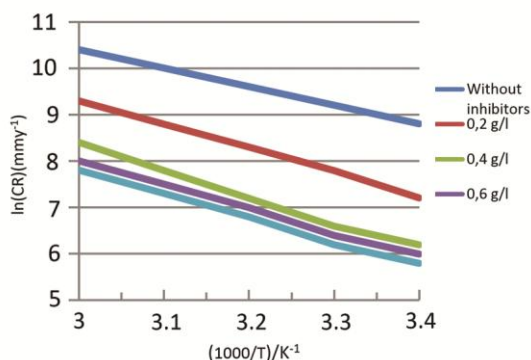| Inhibitor concentration (mg L^{-1})	Temperature (K)	Corrosion rate (g/m^2, days)	Inhibitor efficiency (%)
200	298 K	0,003175	71,56
	313K	0,002895	69,36
400	298 K	0,004125	75,46
	313K	0,003765	72,58
600	298 K	0,003117	88,53
	313K	0,002171	83,76
1000	298 K	0,001125	92,38
	313K	0,001156	93,87

Fig. 1 — Arrhenius plots for mild steel corrosion in 0.5 M HCl solution in different concentrations

Here B is a constant depending on the type of metal, R is the universal gas constant, and T is the absolute temperature. Arrhenius plots for mild steel corrosion in 0.5 M HCl solution in different concentrations are shown in Fig. 1. 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.

Using the Arrhenius equation, corrosion at various concentrations was calculated for 0.5 M hydrochloric acid with and without inhibitors as per the Eq. (4) using thermodynamic parameters such as enthalpy (ΔH) and entropy (ΔS).
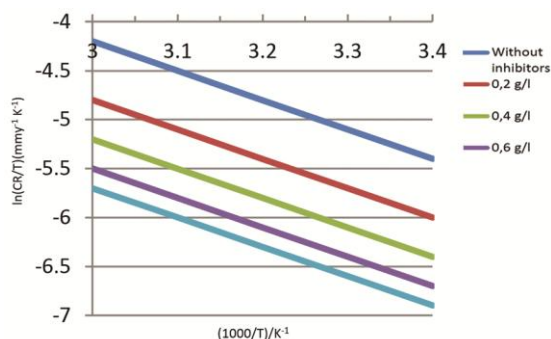
$$\vartheta_{(korr)} = \frac{RT}{Nh} \exp\left(\frac{\Delta S}{R}\right) exp\left(\frac{\Delta H}{RT}\right)$$
… (4)

Here h is Planck's constant, N is Avogadro's number. have a straight line with an inclination = $\Delta H/T$ and intersection 1/T relatively ln (forT) = ln $(R / Nh) + \Delta S / R$.

Dependency plots $1/T$ or $ln(v_{corr}/T)$ for corrosion of metals show the presence of the inhibitor at various concentrations in Fig. 2. The calculated activation parameters are shown in Table 3. If we compare the activation energy (E_a) of the solution used with the inhibitor with the solution used without the inhibitor, we can see that the addition of the inhibitor (E_a) to the

Table 3 — Parameters of activation of 0.5 M hydrochloric acid at various inhibitor concentrations

Inhibitor concentration (gL^{-1})	E_a (kJ mol^{-1})	ΔH_a (kJ mol^{-1})	ΔS_a (kJ mol^{-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

Fig. 2 — Diagrams 1/T for ln (v$_{corr}$/T) corrosion of steel in 0.5 M HCl containing various inhibitor concentrations

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.

As shown in Table 3, the values of activation energy (E_a) 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 this phase 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 [26,27].

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].

Table 4 — Inhibitory and non-inhibitory parameters of the Langmuir adsorption isotherm for carbon steel in an acidic environment of 0.5 M HCl at a concentration of 1 g L^{-1}

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

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. The term *(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 (Fig. 3) is represented by the following Eq. (5) [28-29].

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

where *C* is the inhibitor concentration, θ is the degree of surface coverage, and k_{ads} is the adsorption equilibrium constant. Mass loss and electrochemical results are measured by the adsorption characteristics of the process. The Temkin isotherm (Fig. 4) is represented by the equation below as in Eq. (6).

$$\theta = \frac{-\ln k_{ads}}{2a} - \frac{\ln C}{2a} \qquad ... (6)$$

In the above equation, the adsorption equilibrium constant k_{ads} and the parameters acting on "a" value.

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

$$\Delta G°_{ads} = -RT\ln(k_{ads} x p_w) \qquad ... (7)$$

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

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 *ΔG°_{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^{-1} is the equilibrium state of chemical and physical adsorption. It is assumed that *ΔG°_{ads}* represents the physical absorption if the value
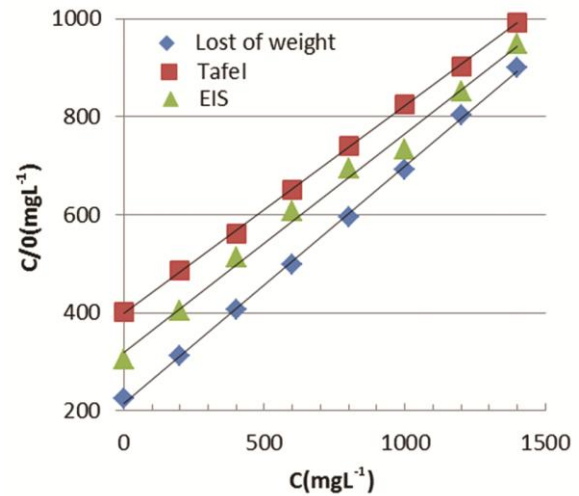

Fig. 3 — For carbon steel structures in 0.5 M HCl acid 1 g/L with and without inhibitors. Langmuir adsorption isotherm
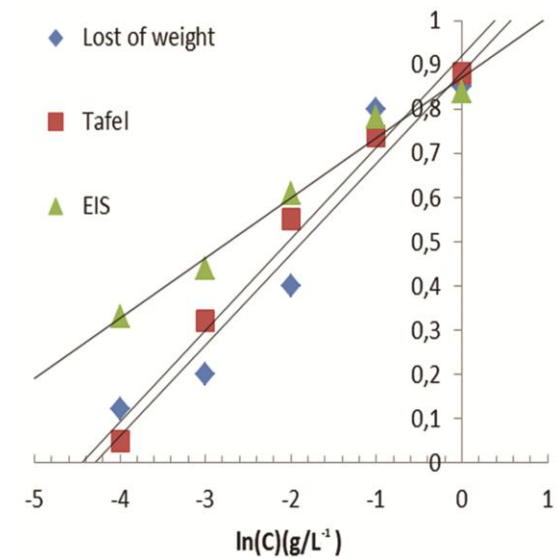

Fig. 4 — Inhibitor and non-inhibitor parameters of 1 g/L concentration for 0.5 M hydrochloric acid medium for carbon steel

is less than -20 kJ mol^{-1}, and the chemical value if the *ΔG°_{ads}* value is more negative than 40 kJ mol^{-1}.

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 [30-31]. When determining the morphological structure of the metal surface, the samples were examined using a scanning electron microscope. Fig. 5a shows the SEM analysis of the surface of a metal sample before the experiment. Fig. 5b shows an example of a steel sample in 0.5 M HCl solution without inhibitors after 120 h. Fig. 5c shows a surface view of a 0.5 M HCl 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.

A model of the two mechanisms described above is shown in Fig. 6. 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 physical and chemical adsorption based on van der Walls forces, play an important role.
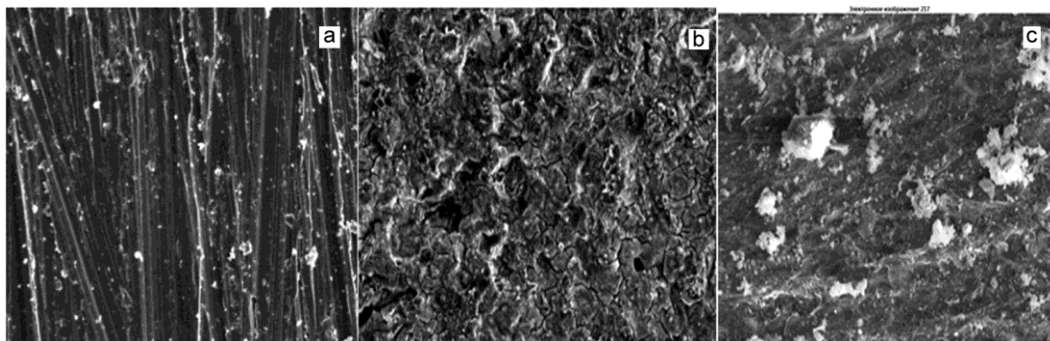

Fig. 5 — SEM images of (a) initial sample steel, (b) steel sample immersed in 0.5 M HCl without inhibitors, and (c) steel immersed in 0.5 M HCl in the presence of *Salsola oppositifolia* extract
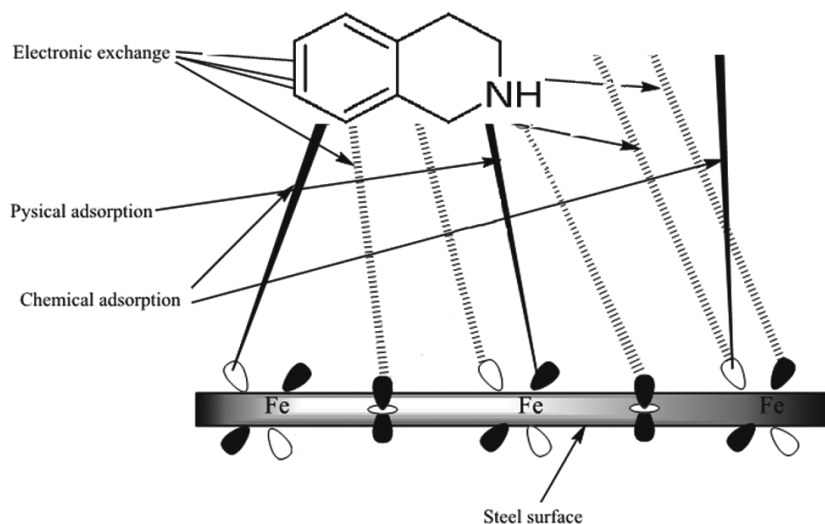

Fig. 6 — Corrosion protection mechanism

Conclusion

Results shows that the extract of the *Salsola oppositifolia* is a very high effective when use as a green inhibitor up to 93.87% at a temperature of 313 K. 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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