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EVALUATION OF THE PROTECTIVE EFFECTIVENESS OF AQUEOUS PLANT EXTRACTS IN THE COMPOSITION OF CORROSION INHIBITOR EXTRACT

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Abstract. An urgent scientific and technical task is the study of corrosion processes and finding cheap and effective methods of protection. As a result of corrosion destruction, about 10% of annual metal production is lost. Therefore, considerable attention is paid to anti-corrosion measures. Rust inhibitors are an effective way to remove rust and protect against corrosion. Recently, the so-called "green inhibitors" have aroused increased interest. Many plants are a source of such inhibitors, a complex of compounds — alkaloids, polysaccharides, proteins, mucous and tannins. All of them, although to varying degrees, have the ability to be adsorbed on a metal surface and fixed on it. We conducted research on the possibility of protecting metals from corrosion with extracts: Tomato edible Lycopersicum, Celandine Chelidonium majus L, Althaea Althaea officinalis L., Yarrow Achillea millefolium.

Key words: green inhibitors, corrosion inhibitors, metal corrosion, plant extracts.

Introduction. Many corrosion inhibitors are now available. All of them, entering into a chemical reaction of the products of thinking on the surface of the metal, which determines the appearance of moisture through the creation of a dense protective film that changes the metal base. The use of all these mixtures, depending on which solution is used, can slow down or stop oxidative processes [1, 3].

A new generation of environmental regulations requires the replacement of toxic chemicals with so-called "green inhibitors". The choice of inhibitor for a particular application is limited by several factors, including increased environmental awareness and the need to encourage environmentally friendly processes in conjunction with the specific actions of most acid inhibitors, which often require the combined action of compounds to achieve effective corrosion inhibition.

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For this reason, in recent years, great efforts have been made in this area to develop new environmentally friendly inhibitors [2–6].

From the point of view of environmental friendliness, promising components of protective materials can be products of plant origin, one of the main advantages of which is relative cheapness and fast renewability. In the last two decades, research has been carried out to find and obtain the so-called “green” inhibitors: cheaper, readily available and reducing the risk of environmental impact [7].

Sources of such substances can be non-toxic and renewable plant waste. Sources describe extracts of a number of plants that exhibit inhibitory properties to various metals, but the mechanism of their action is practically not studied [8–10].

An extract is a solution consisting of active substances from the whole plant or its parts (roots, leaves, flowers, fruits) and a liquid part that acts as a solvent. The concentration of the extract depends on the solvent and its polarity, the method of extraction. The solvent is most often water or ethyl alcohol.

Various substances have been used since ancient times to prevent corrosion processes. In the Middle Ages, gunsmiths, removing scale from steel, added starch and brewer’s yeast to acid solutions. In the 1900s and 1930s, patented inhibitors were starch, dextrin, gelatin, casein, cake, molasses, carbohydrates, and extracts of wood and coal resins. There are now many developments to protect various alloys with aqueous or alcoholic plant extracts. In table 1. presents some plant extracts as inhibitors that have been studied over the past 10 years. These extracts have been proposed to protect certain metals and alloys.

Table 1. **Extracts of plant origin which are created to protect metals**

Plant extracts are alcohol or water	Metal that is protected
Mexican tea, fragrant osmanthus leaves, Chinese hibiscus, turmeric long, three-toothed larry	Carbon steel
Garcinia seeds, pointed banana flowers, Mexican argemon, lavender, peppermint, bark and leaves of kadamba, leaves of Kenning ants, roselle, Chinese lemongrass, citrus larch leaves	Low carbon steel
Hemp	Copper
Wormwood oil	Steel
Tannin of a mangrove tree, vernonia, fruit juice date, garlic, prickly pear Indian, tobacco	Aluminum

Continuation of table 1

onion juice	Zinc
ordinary grenade	Brass
lavender	Stainless steel

Reagents and equipment. During the research the following utensils and equipment were used: volumetric flasks, beakers, spatulas, filter paper, petri dishes, laboratory electronic analytical scales VLA-200 (d = 0.001 g), drying cabinet, multifunctional device EZODO.

The following reagents were used in the course of work: natural sea salt, sea salt solution with a concentration of 16‰of distilled water, aqueous solution of 2 mol / l hydrochloric acid. All solutions were prepared on distilled water.

For the study, we also used extracts in two different solvents. The solvents were water and ethyl alcohol. Extracts were also prepared in two ways: from fresh raw materials and from dry raw materials. The extraction was performed directly. First, the plants were weighed and crushed. Then poured the solvent and defended for 5 days in a dark place, periodically stirring the contents.

Experiment techniques. The following research methods and calculations were used during the research. Method of obtaining pickling solutions (Holgin method): plant raw materials (leaves and stems) of wild or domestic plants were crushed with a knife and filled with a weak, concentration of not more than 5%, hydrochloric acid solution. Left for extraction for 7 days. 8 samples were made: option A from fresh plants, option B from dry raw materials. When the extract was ready, a pickling solution was prepared to study its effectiveness.

The protective effect of inhibitors, ie their ability to inhibit the corrosion rate, is evaluated by the inhibition coefficient (g) and the degree of protection (Z). The density of the inhibitor solution was taken equal to the solvent.

All test samples had a thickness of 1 mm. Corrosion losses were evaluated by the gravimetric method on the weight loss of the sample during corrosion. The values of the protective effect of the coating were calculated by the formula:

$$\mathrm{Km} = \frac{\mathrm{m}_1 - \mathrm{m}_2}{\mathrm{S} \cdot \tau}$$

where Km — corrosion rate, $\mathrm{g}/\left(\mathrm{cm}^2 \cdot \mathrm{h}\right)$; m_1 — mass of the sample before the test, g; m_2 — mass of the sample after the test, g; S — surface area of the sample, cm^2; τ — duration of the study, (hour).

The film thickness was estimated gravimetrically, assuming that the layer is evenly distributed:

$$h = \frac{(m - m_0) \cdot 1000}{S \cdot \rho}$$

where h is the film thickness, μm, m is the mass of the sample with the film, g, m_0 is the mass of the sample without the film, g, ρ is the density of the composition, g/cm, S is the area of the sample, cm.

The effectiveness of the protective action of the corrosion inhibitor was evaluated by the degree of protection:

$$Zm = \frac{Km - K'm}{Km} \cdot 100,\ \%,$$

where Km, K'm — corrosion rate of the metal without inhibitor and with inhibitor, respectively, g/ $\left(cm^2 \cdot hour\right)$.

The presence of the effect of "aftereffect" was checked after treatment of steel samples with a disinfectant solution of 1 mol / l hydrochloric acid with the addition of test inhibitors at the optimal concentration of 0.5 g / l for some time. Untreated control plates were immersed in a corrosive working medium without inhibitor, kept. After exposure, the plates were washed with water, weighed and calculated the degree of corrosion protection. The anti-corrosion effect provides the presence of a film on the metal surface formed by adsorption of the inhibitor.

For the experiment, samples were taken from steel (composition, wt.% Fe — 98; C — 0.17–0.24; Si — 0.17–0.37; As — 0.08). Plates in the size of 50 mm*100 mm, 1 mm thick. To assess the protective effectiveness of the solutions, steel samples were polished, degreased with ethyl alcohol, weighed. The film was applied by immersing the samples in the test pickling solution at room temperature for 1 minute, followed by drying in an upright position for 10 minutes in an oven. Corrosion losses were evaluated by gravimetric method on the loss of mass of the sample during corrosion. We studied the effectiveness of the inhibitory effect of aqueous extracts of plants: edible tomato, yarrow, celandine.

Studies on corrosion resistance were performed at a temperature in the range of 19–23°C. Weight loss and hydrogen evolution are most often used to assess corrosion inhibition and the effectiveness of experimental "green inhibitors".

The values of the protective effect of the coating were calculated by the formula:

$$Km = \frac{m_1 - m_2}{S \cdot \tau}$$

Results and its discussion. Having received the results and analyzing them, we can say that the proposed extracts are quite good at protecting the metal from aggressive environments. The effectiveness of the protective action of the proposed inhibitors shown in tables 2–4.

Table 2. **The magnitude of the protective effect of the coating in an acidic environment**

K. sampel / hour	1 hour	24 hour	48 hour	96 hour
Km 0	0.003214	-0.085714286	-0.085714	-0.377143
Km 1 a	0.001429	-1.808571429	0.6428571	3.7028571
Km 1 b	0.002143	-1.808571429	0.54	4.8
Km 2 a	0.002857	-1.311428571	-0.145714	4.3885714
Km 2 b	-0.00071	-1.56	1.1485714	0.1714286
Km 3 a	-0.00393	-0.771428571	0.2657143	1.5085714
Km 3 b	-0.0025	-0.874285714	0.1457143	2.9142857
Km 4 a	-0.00357	-0.994285714	0.2914286	2.4
Km 4 b	-0.00536	-1.037142857	0.1457143	3.0514286

Table 3. **The magnitude of the protective effect of the coating in seawater**

K. sampel / hour	1 hour	24 hour	48 hour	96 hour
Km 0	-0.000831	0.812775	0.313125	3.9189
Km 1 a	-0.000459	0.020925	-0.00525	-0.0093
Km 1 b	-0.000681	0.01785	-0.00217	-0.0102
Km 2 a	-0.0004	0.024525	0.003075	0.1803
Km 2 b	-0.000581	0.02295	-0.0018	-0.0057
Km 3 a	-0.000419	0.020175	-0.06975	-0.066
Km 3 b	-0.000275	0.023775	-0.00592	-0.1221
Km 4 a	-0.000497	0.01965	-0.00075	-0.0396
Km 4 b	0.0001437	0.028125	-0.00135	-0.0057

Table 2 shows the results of immersion of inhibitor-treated plates in hydrochloric acid solution. Table 3 shows the results of the study in seawater. The seawater solution was modeled with sea salt from the Black Sea.

Therefore, the concentration of the solution was adjusted to the main salinity of the sea in 16‰. The analysis was performed at constant temperature.

The electrolyte concentration at each step was monitored by electrical conductivity using an EZODO multifunction instrument. Measurements showed that during the long stay of the metal in the experimental solution, the concentration did not change significantly, so we can assume that the solution had approximately the same concentration of electrolyte.

It is established that the main components of plant raw materials used for extraction of corrosion inhibitors are glycosides: sucrose, guanosine, xanthonosine; purple aldehyde, ketone 3,5-dimethoxyacetophenone, steroids and saturated and unsaturated fatty acids, represented by palmitic, oleic, linoleic and acetic acids [9–13].

Given the fact that inhibitors now have high environmental requirements, inhibitors based on plant extracts are becoming increasingly popular.

According to the method of corrosion inhibition, corrosion inhibitors can be classified into: cathode, anode, or mixed type inhibitors [14–16]. Cathodic corrosion inhibitors reduce the corrosion potential, anodic corrosion inhibitors move the corrosion potential towards higher value. Mixed inhibitors can protect the metal by physicosorption, chemisorption and film formation [14–16]. Physical sorption occurs due to electrostatic interaction between inhibitor molecules and the metal surface. Chemisorption occurs due to donor-acceptor interaction between vacant orbitals on the metal surface and free electron pairs that have an inhibitor [14–16]. Most of the ingredients derived from plant extracts adsorbed on metal according to the Langmuir adsorption model.

The effectiveness of the protective action of the corrosion inhibitor was evaluated by the degree of protection:

$$\mathrm{Zm} = \frac{\mathrm{Km} - \mathrm{K'm}}{\mathrm{Km}} \cdot 100,\ \%,$$

The data obtained after the calculation are presented in table 4.

Table 4. **The effectiveness of the protective action of the inhibitor**

Zm	hour	24	48	96
1 а	55.55556	-2010	850	1081.8182
1 б	33.33333	-2010	730	1372.7273
2 а	11.11111	-1430	-70	1263.6364
2 б	122.2222	-1720	1440	145.45455

Continuation of table 4

3 a	222.2222	-800	410	500
3 б	177.7778	-920	270	872.72727
4 a	211.1111	-1060	440	736.36364
4 б	266.6667	-1110	270	909.09091

We also calculated the cost of a household corrosion inhibitor. According to the degree of impact on the body, hydrochloric acid belongs to the substances of the 3rd class of danger. HCl — 12%, from 7 gr. liter is not a precursor, in free sale. Vegetable raw material is a waste product or is considered a weed — (free) 350 g. According to the results of calculations per liter of 13% solution, you can prepare 2.769 liters of pickling solution, which can protect 31013 m^2 of steel surface. Therefore, this type of inhibitors is affordable and their preparation does not require special user training. The technique is easy to perform.

We offer environmentally friendly and cost-effective corrosion inhibitors of low-carbon steels based on vegetable raw materials — Edible Tomato Lycopersicum, Celandine Chelidonium majus L, Althaea Althaea officinalis L., Yarrow Achillea millefolium.

In an acidic environment when using aqueous extracts of these plants, the degree of protection is 90.11%.

In a solution of sea salt, which contains 16‰of salt content, which corresponds to the concentration and density of water in the Black Sea, the degree of protection is 91.29–93.65%.

During the long stay of metal in the solutions, the concentration of electrolyte did not change significantly, so we can assume that the solution had approximately the same concentration throughout the experiment.

We can assume that the proposed extracts are quite effective.

Conclusions. Various substances have been used to prevent corrosion since ancient times. Today, rust converters are used, which are mostly synthetic. Their main disadvantages: high enough toxicity, which requires careful handling of the liquid and is dangerous to the environment, long drying time, inability to work with a thick layer of rust. Not always gives the desired effect, high price.

To develop effective and environmentally friendly inhibitors, you can use plant raw materials, namely: fresh tops and dried parts of the stem and leaves of Tomato Lycopersicum, Celandine Chelidonium majus L, Althaea Althaea officinalis L., Yarrow Achillea millefolium. The active substances were removed by extraction from the crushed plant material with the appropriate amount of extractant (water, 5% hydrochloric acid solution according to the method of Holguin), followed by filtration and decantation of the supernatant.

During the experimental study of homemade plant inhibitors based on extracts: Tomato Lycopersicum, Celandine Chelidonium majus L, Althaea Althaea officinalis L., Yarrow Achillea millefolium found that the extracts of all studied plants have inhibitory properties. The greatest value of the protective effect of the coating have the extracts of Celandine and dried Tomato edible fresh, slightly less than Althaea dried. The smallest extract of the tops of Tomato edible dried and fresh Yarrow. The effect of protective action, during long-term exposure to aggressive environments, is also greatest in Chitosan ordinary dried and tops of edible fresh tomatoes, slightly less — dried marshmallows. The smallest is the extract of Tomato tops of edible dried and fresh Yarrow.

These results are confirmed by microscopic examinations of the surface of the experimental plates. In an acidic environment when using aqueous extracts of these plants, the degree of protection is 90.11%. In sea salt solution, the degree of protection is 91.29–93.65%.

This version of the study of corrosion inhibitors better understands the process of creating an inhibitor and the conditions of its use. This method can simulate many variants of inhibitors of plant origin. This allows the use of research data to explain and model the concepts of corrosion, inhibitors, and corrosion protection during student learning. When studying the basic concepts of physico-chemical corrosion protection in the course "Physical and colloid chemistry".

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ОЦІНКА ЗАХИСНОЇ ЕФЕКТИВНОСТІ ВОДНИХ РОСЛИННИХ ЕКСТРАКТІВ У СКЛАДІ ЕКСТРАКТУ-ІНГІБІТОРА КОРОЗІЇ

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Анотація. Актуальним науково-технічним завданням є вивчення корозійних процесів і пошук дешевих та ефективних методів захисту. Унаслідок корозійного руйнування втрачається близько 10% річного виробництва металу. Тому антикорозійним заходам приділяється значна увага. Інгібітори іржі є ефективним способом її видалення та захисту від корозії. Останнім часом підвищений інтерес викликають так звані «зелені інгібітори». Багато рослин є джерелом таких інгібіторів, комплексу сполук алкалоїдів, полісахаридів, білків, слизових і дубильних речовин. Усі вони, хоча і в різному ступені, здатні адсорбуватися на металевій поверхні та закріплюватися на ній. Проведені дослідження демонструють можливості захисту металів від корозії за допомогою екстрактів рослин: томата їстівного *Solanum lycopersicum*, чистотілу *Chelidonium majus* L., *Althaea officinalis* L., деревію *Achillea millefolium* L.

Ключові слова: зелені інгібітори, інгібітори корозії, корозія металів, рослинні екстракти.

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