

Sage Extracts as Inhibitors of Steel Corrosion in 4% HCl

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In this paper the research of corrosion protection of steel by processing corrosion environment using various concentrations of sage extracts (*Salvia officinalis*) (0.5 g/dm³, 1 g/dm³ and 1.5 g/dm³) in a 4% solution of HCl was carried out. Measurements were performed using gravimetric and electrochemical methods (Tafel extrapolation method and electrochemical impedance spectroscopy). The results have showed that sage is recommendable as a possible inhibitor in 4% solutions of HCl. The research also confirms that electrochemical impedance spectroscopy is a reliable method to use for rapid corrosion tests, since the results confirm the gravimetric measurements of corrosion indicators. Determination of corrosion rate and the degree of protection using Tafel diagrams calculated on the basis of corrosion current did not give reliable results. The results show that sage may be used as a "green inhibitor" for protection of steel in a shorter period of time. The degree of protection ranges up to 64.5% for steel 2; however, since sage is environmentally friendly, it is a suitable corrosion inhibitor for shorter periods of time.

Keywords: steel, inhibitor, corrosion, corrosion indicator, protective factor.

1. INTRODUCTION

Greater efforts for the preservation of the environment have led to the establishment of stricter criteria when it comes to the use of chemicals that have a harmful effect on living things and the environment. This has largely reduced or completely abolished the use of numerous very efficient corrosion inhibitors. The use of amines has been restricted due to their toxicity, whereas arsenic oxides and propargyl alcohol had to be completely replaced with less toxic inhibitors.

Corrosion is a serious problem in modern industry. Metal corrosion costs the modern world a lot of money. Corrosion protection costs are inevitable and its consequences must be removed.

Otherwise, the entire constructions, plants or other materials become unusable in a very short period of time [1-4].

Future researches in this field tend to be focused on obtaining environmentally friendly inhibitors (the so-called “green inhibitors”) of greatest possible efficiency and cost-effectiveness. Green inhibitors should be biodegradable, based on plant or animal origin and they must not contain heavy metals. When it comes to construction materials, environmental acceptability of the inhibitor has been requested for a long time now. However, there is still a lot of room for research in this area. Lately, use of plant extracts as corrosion inhibitors became an area of particular interest for researchers. Extracts are most commonly blends of compounds which contain oxygen, sulfur and nitrogen, which are natural antioxidants and which are cheap and environmentally friendly. The inhibitory effect of the extracts of certain plants is achieved owing to the presence of tannin [5-12].

The aim of this paper is to investigate corrosion stability of steel as the most important construction material, in non-inhibited and inhibited 4% solutions of HCl depending on the time. The corrosion environment was treated with different concentrations of sage extract and the effect of sage on the corrosion rate was investigated. Moreover, the aim was to determine optimal concentration of sage as a corrosion inhibitor in the given environment.

2. EXPERIMENTAL

The experimental part of the research involved using steel samples of known composition whose dimensions were (30x30x1)mm. Inhibitory effect of sage on the corrosion process of the samples was investigated by gravimetric and electrochemical methods in 4% solutions of HCl. All the samples were subjected to chemical treatment, after which corrosion rate was measured in non-inhibited and inhibited solutions. The experiments were performed indoors at room temperature. Before being immersed into corrosion solution, the samples were prepared in an identical way: they were degreased by means of a detergent, rinsed with tap and distilled water, chemically degreased for 20 minutes at the temperature of 80-90 °C in the following solution ($c(\text{NaOH}) = 30 - 40 \text{ g/dm}^3$; $c(\text{Na}_2\text{CO}_3) = 40 - 50 \text{ g/dm}^3$, $(\text{Na}_3\text{PO}_4 \times 10\text{H}_2\text{O}) = 3 - 5 \text{ g/dm}^3$). The samples were rinsed afterwards with tap and distilled water and immersed in corrosion solution (20% H_2SO_4 in the time interval of $\tau = 1 \text{ min}$ at the temperature of 60-70°C). After corrosion, the samples were rinsed with tap and distilled water and 96% ethanol, and then dried. Drying period was 5 minutes and it was performed using a fan heater. After that, the samples were measured. Measured mass represented a starting mass of the sample prior to corrosion.

After measuring, the surface of the samples was activated using 20% H_2SO_4 at $t = 60 - 70^\circ\text{C}$ and $\tau = 2\text{s}$. The sample was then rinsed with tap and distilled water and immersed in inhibited and non-inhibited solutions. Two types of steel were used for experimental part of the research.

Chemical compositions of investigated steels are as follows:

| Steel 1 | C | Si | Mn | P | S | Al |
|---------|-------|------|-------|------|-------|-------|
| % mass. | 0.048 | 0.01 | 0.266 | 0.01 | 0.011 | 0.050 |

| Steel 2 | C | Si | Mn | P | S | Al |
|---------|------|-------|-------|------|-------|-------|
| % mass | 0.04 | 0.004 | 0.192 | 0.01 | 0.008 | 0.038 |

Sage extract was obtained by extracting sage with alcohol (96% CH₃-CH₂-OH).

The extraction involved using following materials:

1. Dried sage,
2. Alcohol i.e. 96% ethanol- CH₃-CH₂-OH,
3. Extraction vessel,
4. 1000cm³ glass vessel with a lid,
5. Funnel,
6. Filter paper.

Obtained extract (calculated as dry matter) was added to a 4% solution of HCl in different concentrations. Thus the following solutions were prepared for the investigation of steel corrosion:

- Solution 1. HCl 4%;
- Solution 2. HCl 4% + 0.5 g/dm³ of sage;
- Solution 3. HCl 4% + 1.0 g/dm³ of sage;
- Solution 4. HCl 4% + 1.5 g/dm³ of sage;

Based on the mass loss in steel samples for the time spent in prepared solutions, negative mass index of corrosion K_m^- , pit depth corrosion indicator, π , and degree of efficiency (degree of protection of the inhibitor) z were calculated. Apart from that, average values of $\overline{K_m^-}$, $\overline{\pi}$, \overline{z} were calculated for all the samples. .

Electrochemical measurements were conducted using potentiostat/galvanostat /ZRAGamrySeriesGTM. Polarization curves were obtained with a scan rate of 0.01 V/s in the range of ± 250 mV for Tafel diagrams vs. the E_{corr} of the working electrode of the measuring solution and measured against the SCE. Impedance measurements were carried out at the constant value of E_{corr} after the electrode had been immersed 2, 4, 6 or 24 h in the test solutions. The frequency range applied was 0.2Hz to 300000Hz. The A.C. signal was 10 mV peak-to-peak with 7 data points per decade.

3. RESULTS AND DISCUSSION

Numerous plant extracts as steel corrosion inhibitors can be found in literature [13-21]. However, most of the green corrosion inhibitors experiments were done on stainless steels [13-15, 19, 21]. The efficiency of sage as a corrosion inhibitor on different steels was investigated by electrochemical methods. Extrapolation method was used for measuring the rate of corrosion (Tafel diagrams were recorded) which served to calculate corrosion potential and corrosion current density. Nyquist curves were also recorded using the means of *electrochemical impedance spectroscopy (EIS)*

Figure 1 shows dependence between negative mass index of steel 1 corrosion and the time of immersion in Solutions 1-4.

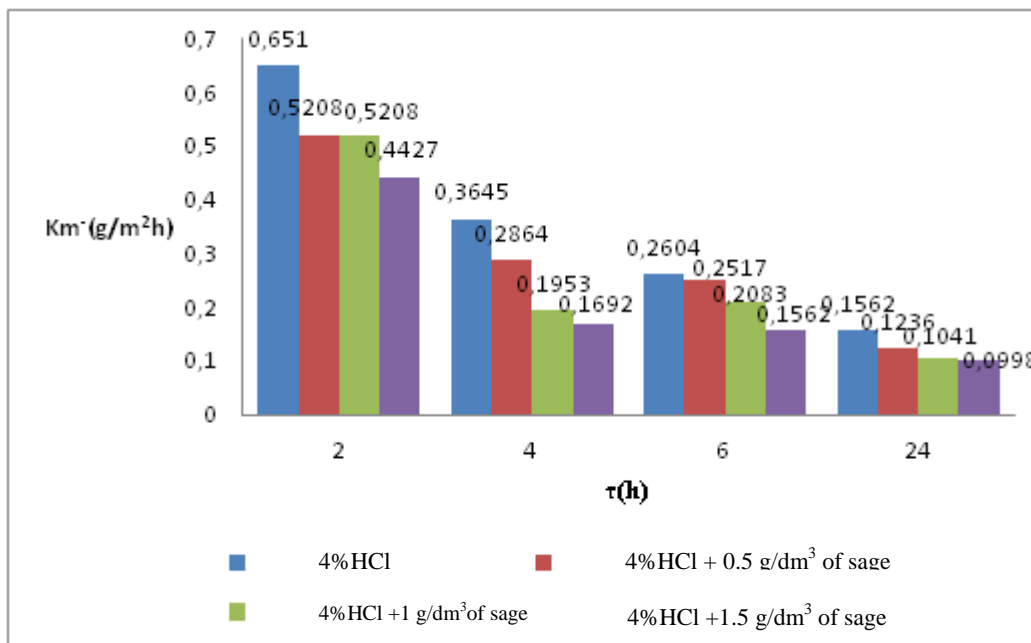


Figure 1. Diagram of negative mass index of corrosion of steel 1 depending on time in Solutions 1-4

Table 1 shows the values of steel corrosion indicators in Solutions 1-4.

Table 1. Steel 1 corrosion indicators in Solutions 1-4

| Corrosion indicator | Solution 1 4% HCl without inhibitor | | | | Solution 2 4% HCl+0.5g/dm ³ of sage | | | | Solution 3 4% HCl+1g/dm ³ of sage | | | | Solution 4 4% HCl+1.5g/dm ³ of sage | | | |
|------------------------------------|---|--------|--------|--------|--|--------|--------|--------|--|--------|--------|--------|--|--------|--------|--------|
| | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 |
| τ(h) | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 |
| Δm(g) | 0.0025 | 0.0028 | 0.003 | 0.0072 | 0.0020 | 0.0022 | 0.0029 | 0.0057 | 0.0020 | 0.0015 | 0.0024 | 0.0048 | 0.0017 | 0.0013 | 0.0018 | 0.0046 |
| K_m^- (g/m ² h) | 0.6510 | 0.3645 | 0.2604 | 0.1562 | 0.5208 | 0.2864 | 0.2517 | 0.1236 | 0.5208 | 0.1953 | 0.2083 | 0.1041 | 0.4427 | 0.1692 | 0.1562 | 0.0998 |
| \bar{K}_m^- (g/m ² h) | 0.3582 | | | | 0.2956 | | | | 0.2571 | | | | 0.2170 | | | |
| z(%) | 0 | 0 | 0 | 0 | 20 | 21.4 | 3.33 | 20.83 | 20 | 46.42 | 20.02 | 33.33 | 32 | 53.57 | 40 | 36.11 |
| \bar{z} (%) | 0 | | | | 16.3075 | | | | 29.9425 | | | | 40.42 | | | |
| π(mm/year) | 0.5914 | 0.3311 | 0.2365 | 0.1418 | 0.5914 | 0.3311 | 0.2365 | 0.1123 | 0.4731 | 0.1774 | 0.1892 | 0.0946 | 0.4021 | 0.1537 | 0.1419 | 0.0906 |
| $\bar{\pi}$ (mm/year) | 0.3252 | | | | 0.3178 | | | | 0.2335 | | | | 0.1971 | | | |

It can be seen from Figure 1 that there is no considerable decrease in value of negative mass index with time increase and with the increase of the sage concentration. The smallest mass loss in steel 1 was in Solution 4 after 24 h.

Figure 2 shows the dependence between depth corrosion indicator in steel 1 and time in Solutions 1-4.

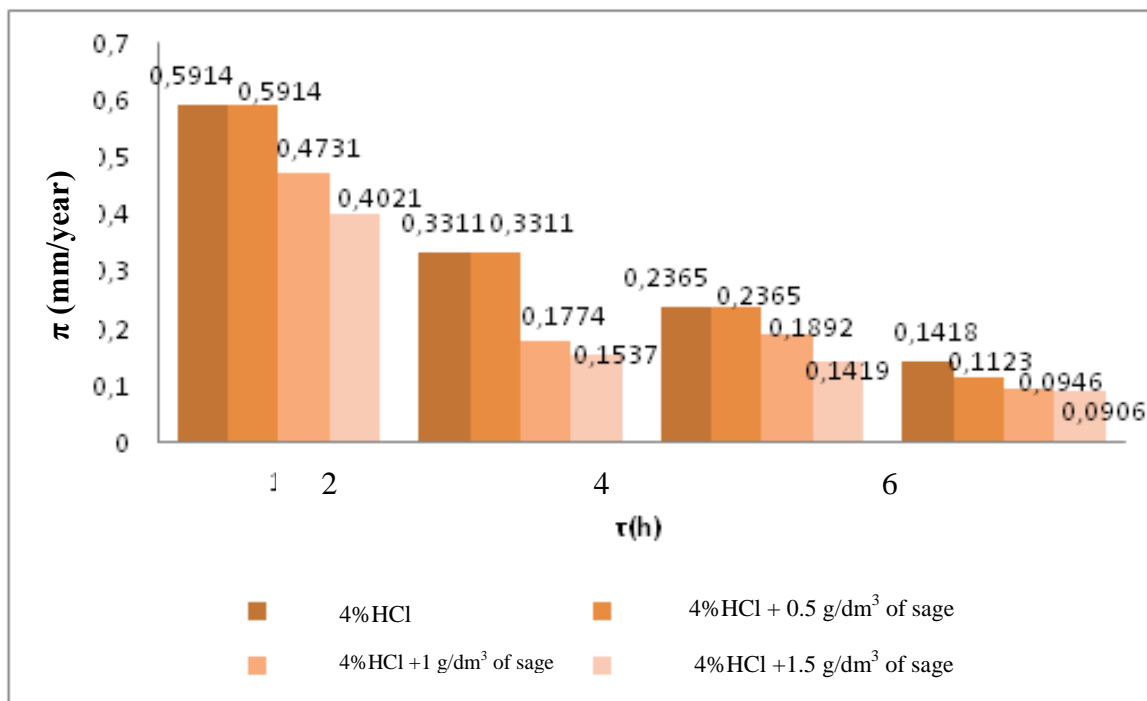


Figure 2. Diagram of depth corrosion indicator in steel 1 depending on time in Solutions 1-4.

Figure 2 shows that the value of depth corrosion indicator in steel 1 in Solutions 1-4 decreases considerably with time as well as with the increase of the sage concentration. The highest values of depth corrosion indicator are in Solution 1 for all the time intervals investigated. It can also be seen that the lowest depth corrosion indicator in steel 1 is in Solution 4 (with 1.5 g/dm³ of sage) after 24h. This indicates that, with time and sage concentration increase, the surface of steel is passivated and corrosion rate decreases. The values of π are similar for all the solutions after time of immersion of steel 1 for 6h and 24h. Thus the average value of π̄ after 6h was 0.2335 mm/year, and after 24h π̄ = 0.1971 mm/year. With the increase of immersion time for steel 1 that is longer than 6h, the value of depth indicator does not change significantly.

Figure 3 shows a diagram of protective factor z(%) depending on time in Solutions 1-4.

It is evident form Figure 3 that the presence of sage in the Solutions 2-4 leads to the presence of protective factor. The highest value of protective factor, z=53.57%, occurs at the sage concentration of 1.5g/dm³ for the time interval of 4 hours. It is also evident that at the sage concentration of 1.5g/dm³, the highest protective factor occurs for all immersion intervals of steel 1 in the Solutions 2-4. In

literature, higher protective factors can be found for sage as green inhibitor [14,15]. However, these experiments were performed on stainless steels.

Table 2 shows steel 2 corrosion indicators in the Solutions 1-4.

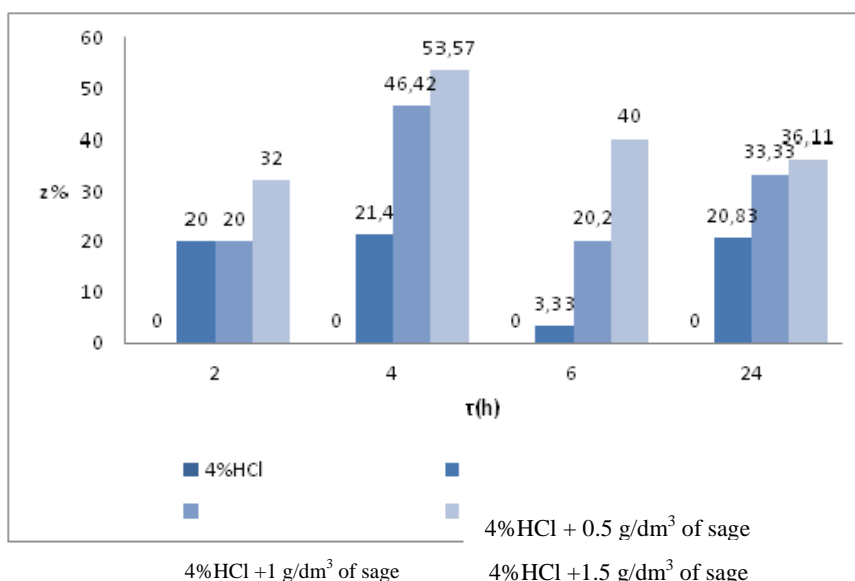


Figure 3. Diagram of protective factor z(%) depending on time in Solutions 1-4.

Table 2. Steel 2 corrosion indicators in the Solutions 1-4

| Corrosion indicator | Solution 1 4%HCl Without inhibitor | | | | Solution 2 4%HCl+0.5g/dm ³ of sage | | | | Solution 3 4%HCl +1g/dm ³ of sage | | | | Solution 4 4%HCl+1.5g/dm ³ of sage | | | |
|------------------------------------|--|--------|--------|--------|---|--------|--------|--------|--|--------|--------|--------|---|--------|--------|--------|
| | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 |
| τ(h) | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 | 2 | 4 | 6 | 24 |
| Δm(g) | 0.0023 | 0.0025 | 0.0048 | 0.0045 | 0.0010 | 0.0010 | 0.0020 | 0.0045 | 0.0012 | 0.0012 | 0.0020 | 0.0040 | 0.0012 | 0.0009 | 0.0017 | 0.0044 |
| K_m^- (g/m ² h) | 0.5989 | 0.3255 | 0.4166 | 0.0976 | 0.2604 | 0.1302 | 0.2604 | 0.0976 | 0.312 | 0.1562 | 0.1736 | 0.0868 | 0.3120 | 0.1171 | 0.1475 | 0.0954 |
| \bar{K}_m^- (g/m ² h) | 0.3596 | | | | 0.1871 | | | | 0.1822 | | | | 0.1681 | | | |
| z(%) | 0 | 0 | 0 | 0 | 56.52 | 60 | 37.5 | 0 | 47.7 | 51.9 | 58.3 | 11.11 | 47.82 | 64 | 64.5 | 2.2 |
| \bar{z} (%) | 0 | | | | 38.505 | | | | 42.25 | | | | 44.63 | | | |
| π(mm/year) | 0.6675 | 0.3993 | 0.5111 | 0.1198 | 0.3194 | 0.1597 | 0.3194 | 0.1198 | 0.3834 | 0.1917 | 0.2130 | 0.1064 | 0.3834 | 0.1437 | 0.1810 | 0.1171 |
| $\bar{\pi}$ (mm/year) | 0.4244 | | | | 0.2299 | | | | 0.2236 | | | | 0.2063 | | | |

Figure 4 shows dependence between negative mass index of steel 2 corrosion and the time of immersion in Solutions 1-4.

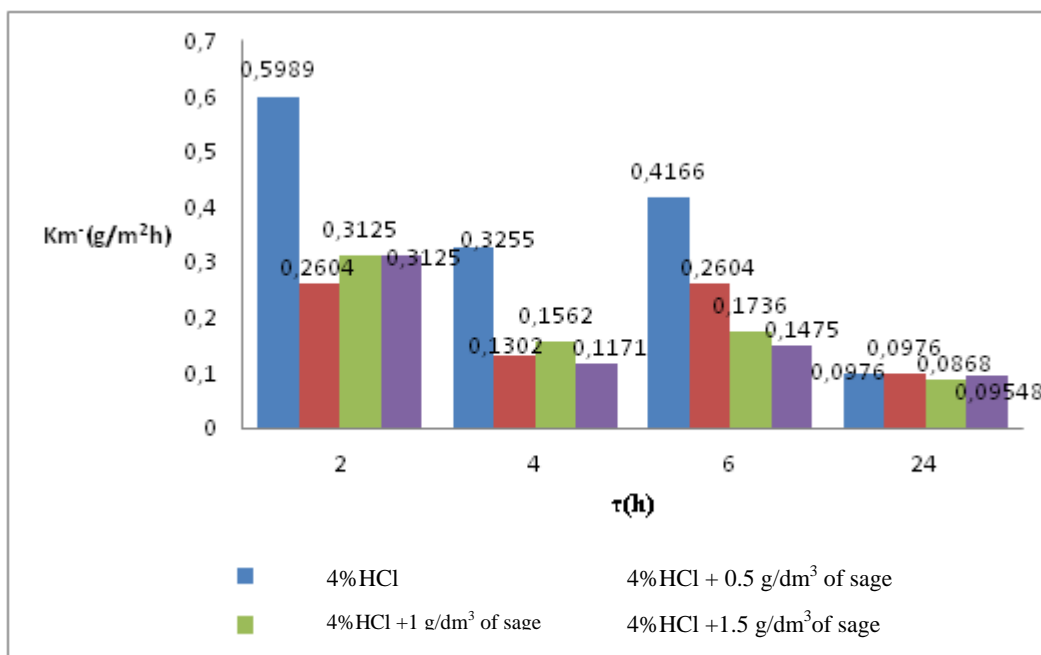


Figure 4. Diagram of negative mass index of corrosion of steel 2 depending on time in Solutions 1-4

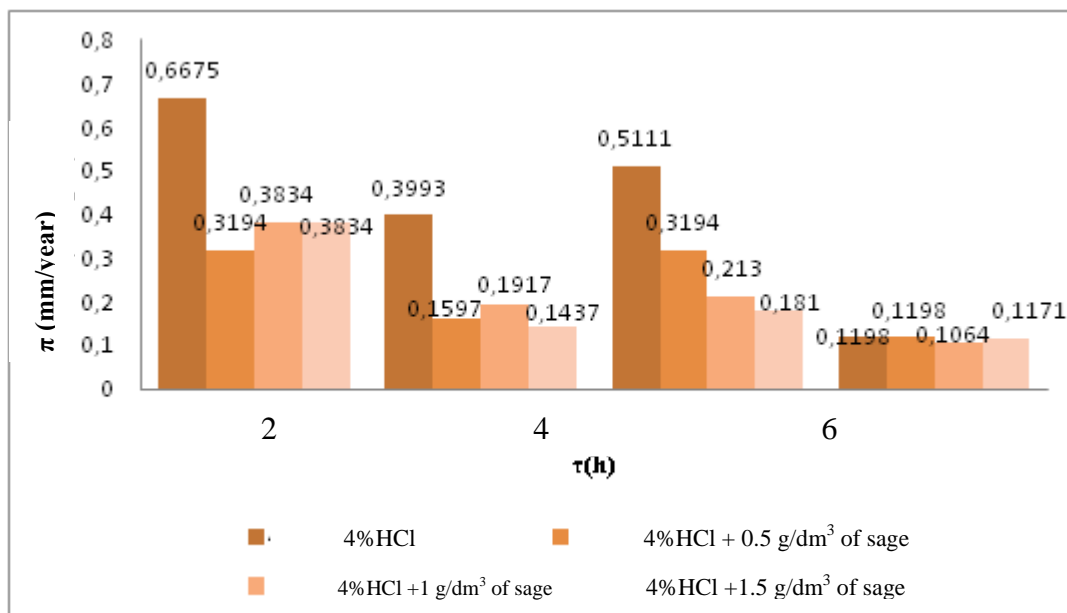


Figure 5. Diagram of depth corrosion indicator in steel 2 depending on time in Solutions 1-4.

It is evident from Figure 4 that the value of negative mass corrosion indicator for steel 2 decreases with time. The lowest value of K_m^- occurs for the time interval of 24h in all Solutions.

Figure 5 shows the dependence between depth corrosion indicator in steel 2 and time in Solutions 1-4.

It can be observed from Figure 5 that the lowest value of pit depth indicator of corrosion is in Solution 4 for all the investigated time intervals, ranging from 0.1064 mm/year to 0.1198 mm/year. Moreover, it is evident that pit depth corrosion indicator decreases with time for all the solutions.

Figure 6 shows a diagram of protective factor of steel 2 corrosion in Solutions 1-4.

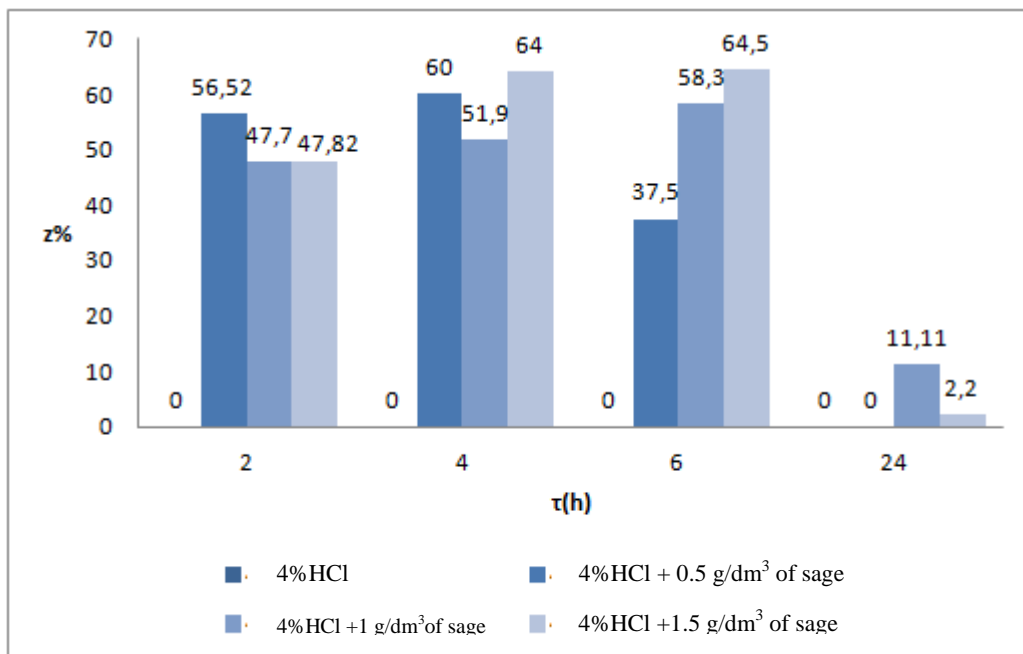


Figure 6. Diagram of protective factor z(%) depending on time of steel 2 corrosion in Solutions 1-4.

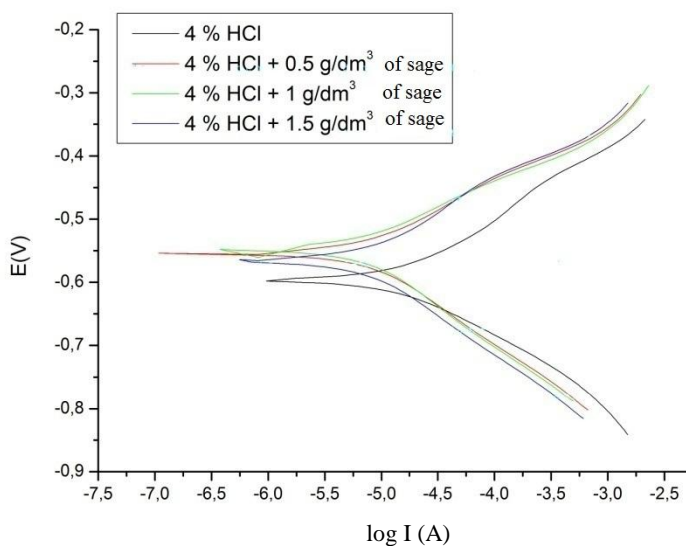


Figure 7. Tafel polarization diagrams for steel 1 in 4% HCl at different sage concentrations.

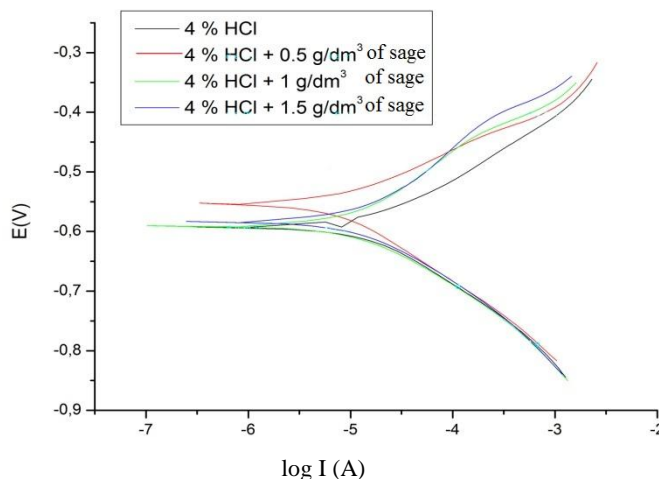


Figure 8. Tafel polarization diagrams for steel 2 in 4% HCl at different sage concentrations.

It can be observed from Figure 6 that the values of protective factor are very similar in Solutions 1-4 for all investigated time intervals. The highest value was obtained after immersion of steel 2 in solution 4 for 6 hours ($\eta = 64.5\%$). These results are in good agreement with the results from the literature [14,15], where stainless steel was used.

Figures 7 and 8 show Tafel diagrams of dependence between (E) and logarithm of the current (log I) in 4% solution of HCl with different sage concentrations.

It can be observed from presented polarization curves that change in sage concentration results in different polarization curves, which indicates that sage concentrations affect the process of corrosion.

Table 3. Calculated values of corrosion potential and corrosion current from recorded Tafel curves for steel 1 and steel 2 in Solutions 1-4

| Solution | Steel 1 | | | | | Steel 2 | | | | |
|--|------------------|------------------------|----------------|-----------------|----------------|------------------|------------------------|----------------|-----------------|----------------|
| | $-E_{corr}$ (mV) | I_{corr} (μA) | b_a (mV/dec) | $-b_c$ (mV/dec) | π (mm/god) | $-E_{corr}$ (mV) | I_{corr} (μA) | b_a (mV/dec) | $-b_c$ (mV/dec) | π (mm/god) |
| 4% HCl | 597.0 | 15.4 | 111.7 | 107.2 | 0.18 | 593.0 | 10.9 | 79.50 | 96.20 | 0.13 |
| 4% HCl + 0.5 g/dm ³ of sage | 554.0 | 7.91 | 107.4 | 130.4 | 0.09 | 554.0 | 7.42 | 78.20 | 115.0 | 0.09 |
| 4% HCl + 1 g/dm ³ of sage | 549.0 | 2.62 | 66.00 | 92.30 | 0.03 | 590.0 | 10.3 | 123.4 | 97.70 | 0.12 |
| 4% HCl + 1.5 g/dm ³ of sage | 566.0 | 9.46 | 133.7 | 150.5 | 0.11 | 583.0 | 11.6 | 125.2 | 105.0 | 0.13 |

Table 3 shows the values of corrosion current and corrosion potential that were calculated using potentiostat/galvanostat /ZRA Gamry Series GTM 750 from recorded Tafel curves. When the data from Table 3 are summarized, it can be concluded that there is no particular dependence between increasing sage concentration and slope of Tafel curves, neither on steel 1 nor steel 2.

It is known from the literature data that applied inhibitors can be qualified as anode or cathode inhibitors if corrosion potential shift is higher than 85 mV compared to the corrosion potential of a sample taken from non-inhibited solutions. This suggests that sage extract acts as a mixed inhibitor considering that the values of corrosion potential do not change significantly in the cathode or the anode direction [22]. The lowest rate of corrosion current was obtained at the sage concentration of 0.5g/dm³, which was calculated from recorded Tafel curves, and it is not coherent with the results obtained by gravimetric method.

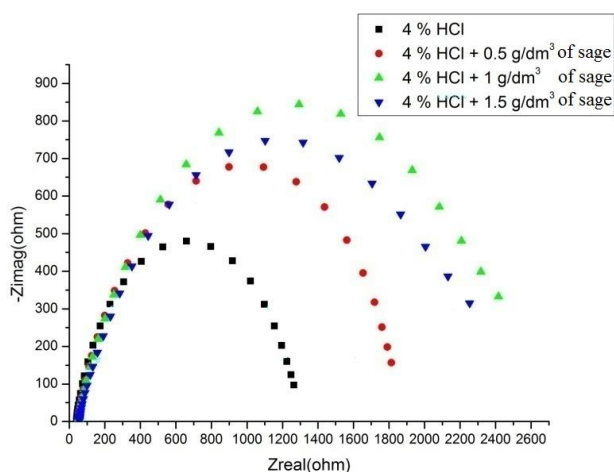


Figure 9. Nyquist curves for steel 1 in Solutions 1-4.

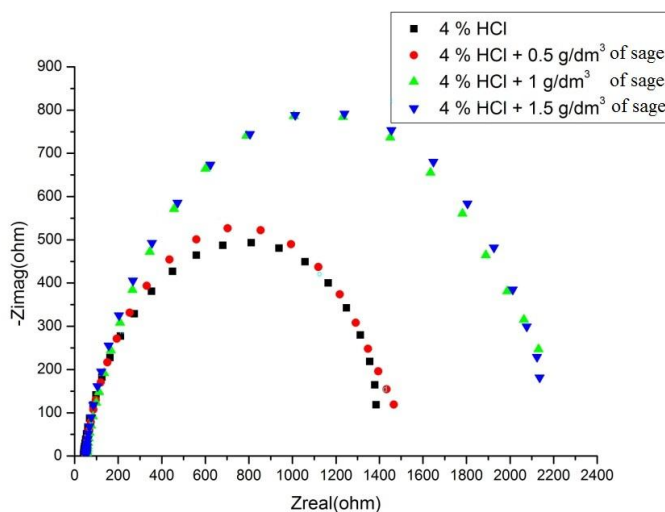


Figure 10. Nyquist curves for steel 2 in Solutions 1-4.

Apart from that, Figures 7 and 8 show that cathode regions of the curves are parallel, which means that adding sage extract into the acid solution did not change the mechanism of hydrogen

formation, and H^+ -ion reduction at the construction steel surface mainly occurs through the mechanism of charge transfer. Therefore, sage extracts are adsorbed on the surface of construction steel, hence blocking the reaction locations. Thus the area available for H^+ -ions is reduced, whereas the actual reaction mechanism remains unchanged [13].

Figures 9 and 10 show the diagrams of dependence of Z_{imag} and Z_{real} (Nyquist curves) which were recorded using *electrochemical impedance spectroscopy* in Solutions 1-4 for both steel 1 and steel 2.

It is evident from Figures 9 and 10 that resistance to corrosion increases with the increase of sage concentration in 4% HCl, which proves that corrosion rate is reduced. The results obtained are coherent with gravimetric measurements of corrosion parameters which also confirm that corrosion is reduced by adding sage and increasing its concentration in 4% HCl. This means that resistance to charge transfer is increased in the presence of sage. The highest corrosion stability for steel 1 is in solution 3 (4% HCl + 1 g/dm³ of sage), and, for steel 2, it is in solution 4 (4% HCl + 1.5g/dm³ of sage).

4. CONCLUSIONS

The highest degree of protection of steel, $\eta=53.57\%$, in 4% HCl occurs at the sage concentration of 1.5 g/dm³ for the time interval of 4 hours, whereas for steel 2 it summons to 64.5% in Solution 4 after 6 hours. The values of average protective factor are approximately the same for steel 1 and steel 2 in Solution 4. Steel 2 has a slightly higher protective factor. The highest average protective factor of steel 2 is in solution 4 ($\bar{\eta} = 44.63\%$). It can be concluded from the obtained results that sage is not a good inhibitor of steel 1 and steel 2 corrosion in 4% HCl, due to the fact that the values of average protective factor $\bar{\eta}$ are below 45%. However, due to its environmentally friendly properties, sage can be used as steel corrosion inhibitor for shorter time intervals.

The results of gravimetric and electrochemical impedance spectroscopy measurements in 4% HCl are coherent, which means that electrochemical impedance spectroscopy can be used as a very reliable method for quick corrosion investigations. Calculation of rate of corrosion and degree of protection using Tafel curves based on the calculated corrosion current do not give reliable results. This can be concluded since the results obtained are incoherent with those which were obtained using gravimetric method and electrochemical impedance spectroscopy (EIS).

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