CORROSION INHIBITION OF MILD STEEL BY *RHUS TYPHINA* LEAF EXTRACT IN HCl SOLUTIONS

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In this study, we evaluate the efficiency of Rhus typhina L. leaves extract to prevent corrosion process of mild steel in HCl medium. It was found using the HPLC method that hydroalcohoolic extracts are rich in polyphenols which act as a protective layer on metal surface. The inhibition efficiency was determined using the weight loss method. The inhibition process is favored by the presence of OH groups and π electrons from aromatic rings.

Keywords: Corrosion inhibitors, plants, extracts, mild steel plates, *Rhus typhina*.

1. Introduction

Corrosion is an important phenomenon where the metals and their alloys undergo transformation in more stable thermodynamically form due to chemical reactions with environmental components [1, 2]: water, bases, acids, salts, gases etc. Costs of corrosion encompass miscellaneous effects related to inefficient materials and energy consumption, enterprises closure or productivity loss and significant concern for human safety as a result of faulty equipment's. Thus, worldwide annual corrosion costs can reach about $2.5 trillion according to NACE report [3]. Iron rusting (a common form of corrosion) occur as follow [4]:

$$\text{Anode: } Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$\text{Cathode: } H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2\ OH^- \quad (2)$$

Ferrous ions are oxidised to ferries ions in presence of dissolved oxygen.

$$2Fe^{2+} + \frac{1}{2} O_2 + H_2O \rightarrow 2Fe^{3+} + 2OH^- \quad (3)$$

$$\textit{Global reaction}: 4Fe\ (s) + 3O_{2\ (g)} + 6H_2O\ (l) \rightarrow 4Fe\ (OH)_3$$

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The process is usually accelerated by activities such as contact with less active metals, acids, stresses in iron and the presence of rust itself. There are several factors that influence the corrosion rate, including diffusion, temperature, conductivity, ion type, pH value and electrochemical potential [5].

Hence, corrosion prevention in a conventional manner involves a diverse array of inhibitors which interrupt the electrochemical cell formed at the metal surface. These inhibitors include inorganic (chromates, nitrates, phosphates, zinc, magnesium etc.) or organic (benzoates, diisopropylammonium, ethanolamine etc.) compounds [6-9]. The use of corrosion inhibitors (CIs) is the most economically viable method, as these materials can be easily applied by batch and/or continuous treatments with minimal amounts of material and with minimal partial or complete shutdown of industrial plants [10, 11].

Despite of their efficiency there is a increasing concern regarding the environmental impact and the effect on human health. Consequently, these compounds were gradually banned and replaced with compounds which comply with green chemistry approach.

The development of green corrosion inhibitors (GCIs) basically focuses on materials that are naturally occurring, easily available, non-toxic, cost-effective, and environmentally friendly. One of the most extensive studies in corrosion protection has been the development of GCIs based on plant extracts. [11-17]. Reports on the use of plant extracts to inhibit corrosion are increasing every year. A growing number of studies also indicate that GCI from plant extracts has great potential for corrosion protection. [11, 18]. The natural compounds found in plant belong to various categories (flavonoids, glycosides, alkaloids, saponins, phytosterols, tannins, anthraquinones, phenolic compounds, terpenes, etc.) and can be used as inhibitors due to their functional groups like amide, hydroxyl, esters, carboxylic, amino etc. Generally, these compounds are poly- and multifunctional therefore these features improve both adsorption on metal surface and hindering the corrosion processes.

A suitable candidate for green inhibitors preparation is represented by plants with proven antioxidant activity and with high content of polyphenols and *Rhus typhina L*. (staghorn sumac) is a good example [19-23]. Native to North America, staghorn sumac is a deciduous shrub or small tree. The fruits are densely packed and have a torch-like shape, and the leaves turn red from autumn onwards [24,25]. Due to its strong adaptability and resilience, it is widely used for revegetation of degraded habitats, and due to its good visual effects, it is also widely used in landscaping. [10]. *Rhus typhina L.* berries have been used extensively throughout history on both the North American and European continents (XI-th century), either for medicinal purposes or as a spice. Studies show that *Rhus typhina L.* fruit extracts had antioxidant properties. These extracts could be utilized as a raw material to create natural antioxidants and/or preservatives for the food industry [26-28]. In

order to obtain these compounds extraction process is performed. One of the modern extraction technique is represented by the microwave-assisted extraction (MAE) [24, 25, 29] which is fast, efficient and with lower solvent consumption.

In this work, extracts of *Rhus typhina L*. leaves collected in autumn were used as green corrosion inhibitor for mild steel plates in hydrochloric acid.

2. Materials and Methods

Vegetal Material

Leaves of Rhus *typhina L*. were harvested in the summer and in the autumn (Fig. 1), thoroughly cleaned to remove foreign parts and were shade dried until constant mass. Vegetal material was grinded and sieved in order to obtain a powder with particles smaller than 0.3 mm.

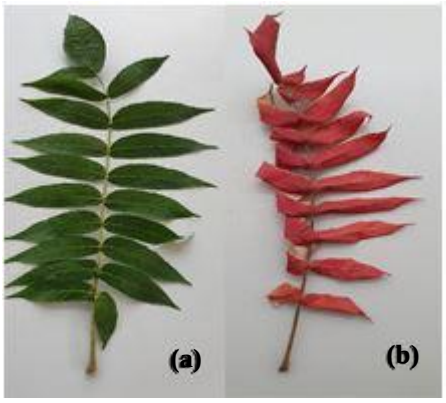

Fig. 1: Leaves of *R. typhina L*. for extract preparation (a) freshly collected (b) dried

Extraction process

The MAE process was performed to extract biologically active *Rhus typhina L*. composed using a microwave extractor (Ethos SEL, Milestone). (Fig. 2). From the homogenized solid sample, 5g of solid material is weighed in teflon vessels. Vegetal material powder was mixed with selected solvent at a ratio of solid: liquid = 1:10 (methanol: ultrapure water = 50:50). The mixture was irradiated for 1 h at 100 °C. After cooling, the extracts are separated from the solid material using 0.2 µm syringe filters (Fig. 3).

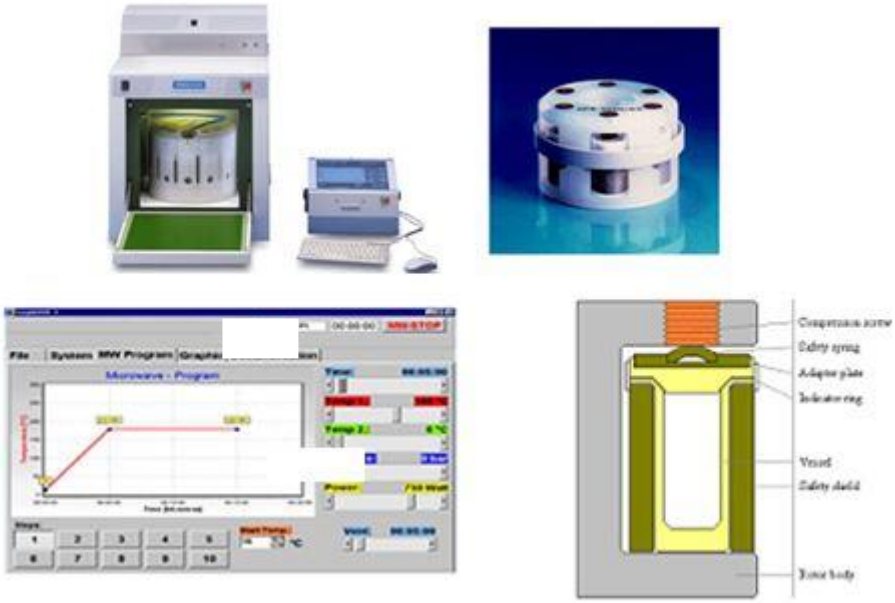

Fig. 2: Microwave extraction system

Fig. 3: Extracts obtained from *Rhus typhina L.* leaves harvested in summer (1) and autumn (2)

Analytical method used for extract characterisation

HPLC-DAD quantification of bioactive polyphenols from Rhus typhina L. extracts was performed. HPLC system L-3000 (RIGOL Technologies, China) equipped with a Kinetex EVO C18 column (150 × 4.6 mm, particle size 5 μm) was used. 20 μL was the volume for the injection process. The solvents used were 0.1 trifluoroacetic acid (TFA) in water and 0.1 TFA in (ACN) acetonitrile. Gradient elution was carried out using TFA in ACN at 30 °C for 60 min and the elution flow rate was set to 1 mL/min. Measurements were executed at λ max 200. Compound

identification and quantification was realised by comparison with standard spectra at each retention time.

Corrosion process set-up

The basic method for determining a metal's corrosion rate is to immerse the sample in the HCl acid medium and measure the weight loss as a function of time. Three MS coupons (*Table 1*) composed of 0.13, 0.18, 0.39, 0.40, 0.04 and 0.025, for C, Si, Mn, P, S, Cu and iron were used.

Tabel 1:

Physical sizes and treatment applied

Sample	Treatment	Dimensions (mm)	Area (mm^2)	Weight (g)
Plate 1	Control	93 x 90 x 2	17472	130.25
Plate 2	Summer leaves extract (SLE)	88 x 91 x 2	16732	124.91
Plate 3	Autumn leaves extract (ALE)	93 x 89 x 2	17282	128.78

Corrosion process was conducted as follow:

- The coupons previously cleaned (washed in high purity water, acetone and then dried) were sprayed with obtained extract, except for one, used as a control;
- Three treatment solutions were prepared (40 mL HCl 1M + 10 mL of extracts or 10 mL ultrapure water for control sample) and poured in Petri plates;
- Metal coupons were immersed in the treatment solutions for 72 hours at 298 K; the plates were mounted on small plastic supports in order to assure complete coverage of with treatment liquid;
- After the treatment, the coupons were extracted rinsed with ultrapure water, acetone, dried and weighted.

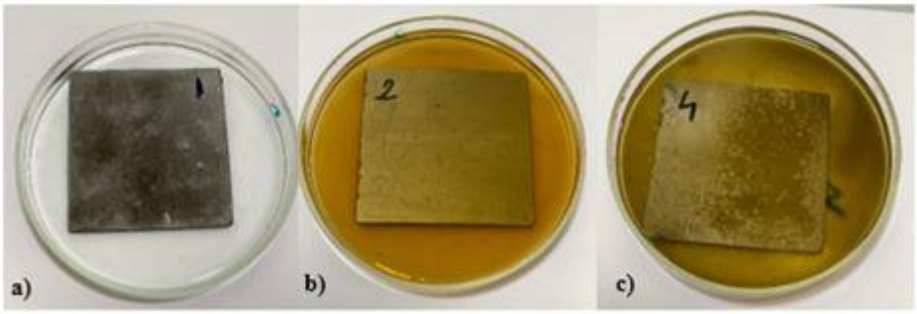

Fig. 4: Metal coupons inserted in treatment solutions: a) control (without extract), b) summer leaves extract;c) autumn leaves extract.

3. Results and Discussion

Characterization of natural extracts

Analysis by HPLC method (Fig.5, Fig.6) reveal the presence of different polyphenols (*Table 2*), with known capacity as corrosion inhibitors. HPLC tests were performed at several wavelengths in order to perform a thorough evaluation of chemical composition and the extract were diluted five times due to the high concentration of the components. In *Table 2*, it can be observed several significant differences between the extract chemical profile, since plant metabolism is changing with weather conditions.

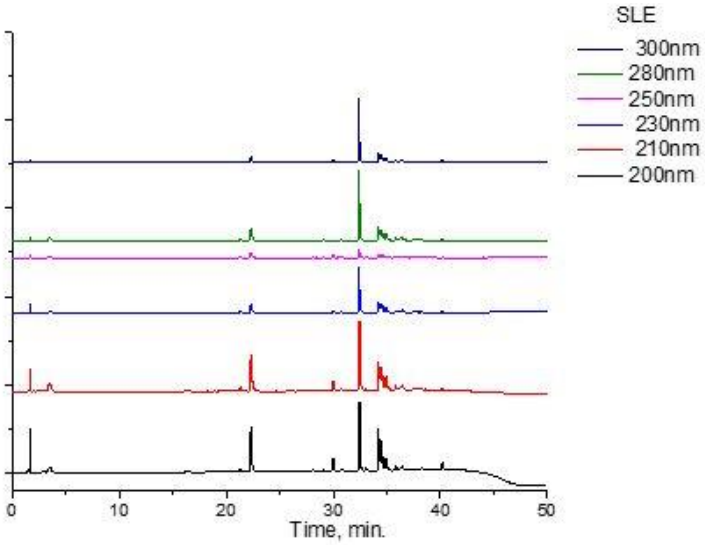

Fig. 5: Chromatograms at different wavelength for ***summer leaves extract (SLE)***

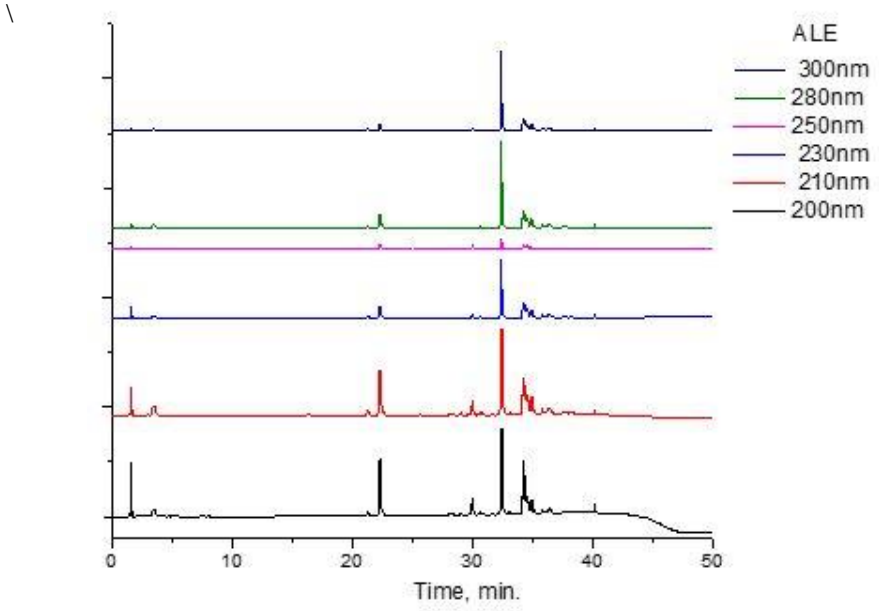

Fig. 6: Chromatograms at different wavelength for ***autumn leaves extract (ALE)***

Table 2:

HPLC Analysis for SLE and ALE

Compounds	**SLE**	**ALE**
Caffeic acid	84.42	-
Chlorogenic acid	1170.61	2049.57
Epicatechin	-	286113.31
Daidzein	14.18	689.49
Hiperoside	129.52	795.37
Rutin	-	6235.85
Naringin	11045.46	233.59
Malvidin	107954.43	25850.76
Quercitin	-	196.80
Naringenin	20.17	274.18
Genistein	21.09	359.59
Gallic acid	625.86	6435.64
p–cumaric acid	4.08	0.00

Characterisation of metal plates

The aspect of metal plates before and after spraying extract is presented in Fig.7; it can be observed the homogeneity of the non-used metal plates (Fig.7.A). A better adherence of the hydroalcoholic extract was obtained for the extract collected in autumn (Fig.7.B3) compared with the one from the summer (Fig.7.B4). This observation is validated by the HCl treatment, wher after 76 hours can be observed a better stability for the autumn extract (Fig.7. C3).

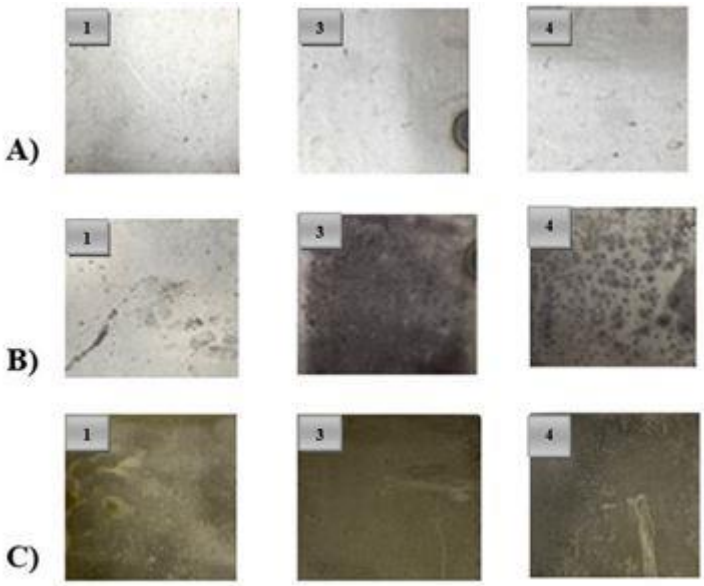

Fig. 7: A) Metal plates before application by spraying extracts, B) Plates immediately after application of extracts by spraying, C) After 76 hours in hydrochloric acid.
Where: 1) Without extract, 3) *Rhus* hydroalcoholic- **ALE**, 4) *Rhus* hydroalcoholic - **SLE**

Weight loss measurements method

Following a 76-hour period, the metal plates were extracted from a 1 M HCl solution, cleaned, and reweighed. The weight losses for each coupon were used to assess the corrosion inhibition capacity of the prepared extract:

$$\Delta m = m_1 - m_2 \quad (5)$$

$$CR = \frac{\Delta m}{A \times t} \quad (6)$$

$$IE\ (\%) \left(\frac{CR_0 - CR_e}{CR_0}\right) x\ 100 \quad (7)$$

Where: CR – corrosion rate, CR_0 - corrosion rate, without extract, CR_e - corrosion rate, with extract, IE – inhibition efficiency

In *Table 3*, it can be observed that mass loss in the control sample was significant higher comparing with protected coupons and corrosion rate is ten time lower for protected samples. Also, it can be noticed that the SLE assure a better protection for metallic plates.

Table 3:

Corrosion rate and inhibition efficiency

Sample	Initial Weight (W_1)	Final Weight (W_2)	Weight Loss ($W_1 - W_2$)	Density (g/cm^3)	Corrosion Rate (CR)	Inhibition Efficiency (IE %)
Control	130.249	129.6667	0.5823	7.78	0.003596	99.744
SLE	128.785	128.7183	0.0667	7.77	0.000728	99.948
ALE	124.915	124.8253	0.0897	7.79	0.001010	99.928

Protection of surfaces can be attributed to the functional groups of polyphenols which interact with occupied orbitals of iron atoms and inducing a chemisorption process (Fig.8). The chelating capacity of these compounds assure a protective layer on the metal surface and hindering the reactions which can occur both in the cathodic and anodic regions.

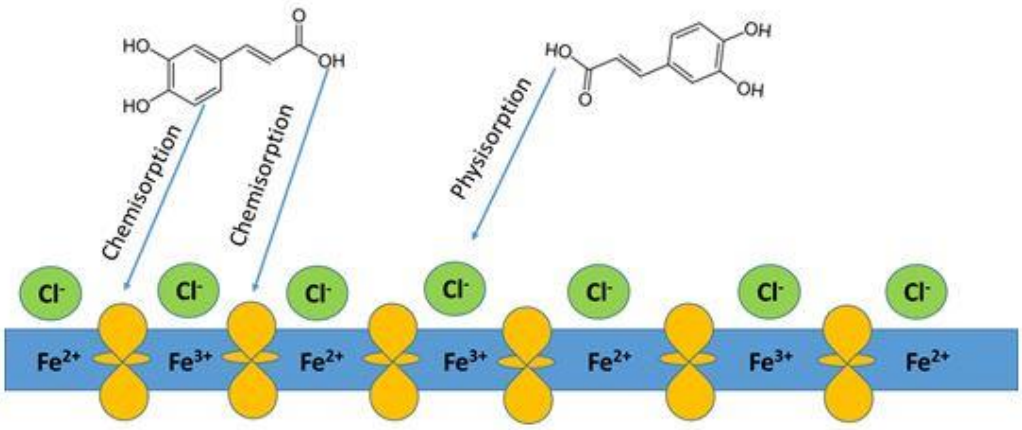

Fig. 8: Protection of surfaces - chemisorption process

4. Conclusions

This work shows that *Rhus typhina L*. leaves extracts contain numerous polyphenols in high concentrations which act very efficiently to inhibit the corrosion of mild steel surface. These compounds act both in cathodic or anodic region thus, the corrosion cell is completely inhibited. The extract from the leaves collected in autumn present a higher concentration of polyphenols comparing with extract from vegetal material collected in summer. The protection process is based on chemisorption and physisorption processes process which occur on the metal surface.

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