



**EXTRACT OF OUTER ONION SKIN, ANOTHER GREEN CORROSION
INHIBITOR FOR ALUMINIUM**

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Abstract

Metal corrosion is a serious problem. It causes serious damage in metallic materials, especially in acid media. We are focused on using green inhibitors, as a good choice for both: corrosion and environment protection. The use of corrosion inhibitors is one of the most practical and economic methods in corrosion inhibition studies. Green inhibitors are biodegradable, environmentally friendly and ecologically acceptable. They do not contain heavy metals or other toxic compounds. One of the green inhibitor is extract of outer onion skin, that content considerable amount of quercetin, among flavonoid compounds on it. In recent years quercetin, is proved to be an efficient inhibitor against the corrosion of metals and alloys. Quercetin is studied as a green corrosion inhibitor, for Aluminium, in acid media (1M HCl). It is extracted by outer onion skin. Quercetin also, has anti-inflammatory, anti-histamine, anti-cancer effects and other biological activities. The corrosion inhibition efficiency of extract from outer onion skin, was investigated using weight loss method and potentiodynamic polarization measurements. By weight loss method the inhibition efficiency (IE) increases with the increase of the inhibitors

concentrations, IE is 44.4 % at 0.75 g/L quercetin. By the potentiodynamic polarization measurements the critical concentration is 1 g/l, IE is 75 %, for the further increase of the concentration the inhibition efficiency decrease.

Key Words: green corrosion inhibitor, quercetin, aluminium, weight loss, potentiodynamic polarization.

1. Introduction

In most industries whose facilities are constituted by metallic structures, the phenomenon of corrosion is invariably present. This problem causes the damage of very important materials and economic losses also, due to partial or total replacement of equipment and structures, and plant-repairing shutdowns. Corrosion is more than just an inevitable natural phenomenon. Corrosion chemistry is changing at a rapid pace and every chemical process is viewed very critically from the points of safety, environmental impact, and economics. Corrosion protect can be very expensive as well as unsafe. One of the methods of combating corrosion is the use of corrosion inhibitors that decrease the corrosion rates to the desired level, with minimal environmental impact. The field of corrosion inhibitors is undergoing dramatic changes from the viewpoint of environmental compatibility. Environmental agencies in various countries have imposed strict rules and regulations for the use and discharge of corrosion inhibitors. It requires, corrosion inhibitors to be environmentally friendly and safe [1, 2]. Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both: human beings and environment. Recent years, increasing of ecological awareness among scientists, have led to the development of “green” alternatives to mitigate corrosion [3]. The use of green inhibitors is one of the best options of protecting metals against corrosion. Several inhibitors in use, are either synthesized from cheap raw material, or chosen from compounds having

heteroatoms in their aromatic or long chain carbon system. However most of these inhibitors are toxic to the environment. In attempt to find corrosion inhibitors which are environmentally safe and readily available, it has been a growing trend, in the use of natural products such as plant extracts, to protect metals and alloys from corrosion, especially in acid media. A lot of works have been reported using the extract of plants, because the low economic cost. This work is focused in extraction of outer onions skins, that content quercetin in considerable amount (about 80%), among the other flavonoid compounds. Flavonoids or also known as secondary metabolites are organic compound found in plants that, are not directly involved in the normal growth, development, or reproduction of organisms. (Fig.1)[4].

Molecules of flavonoids, which are heterocyclic oxygen-containing compounds, include two benzene rings connected with each other by a three-member carbon chain, usually lopped with oxygen. In the molecule of quercetin there are several neighboring hydroxyl groups in the benzene rings.

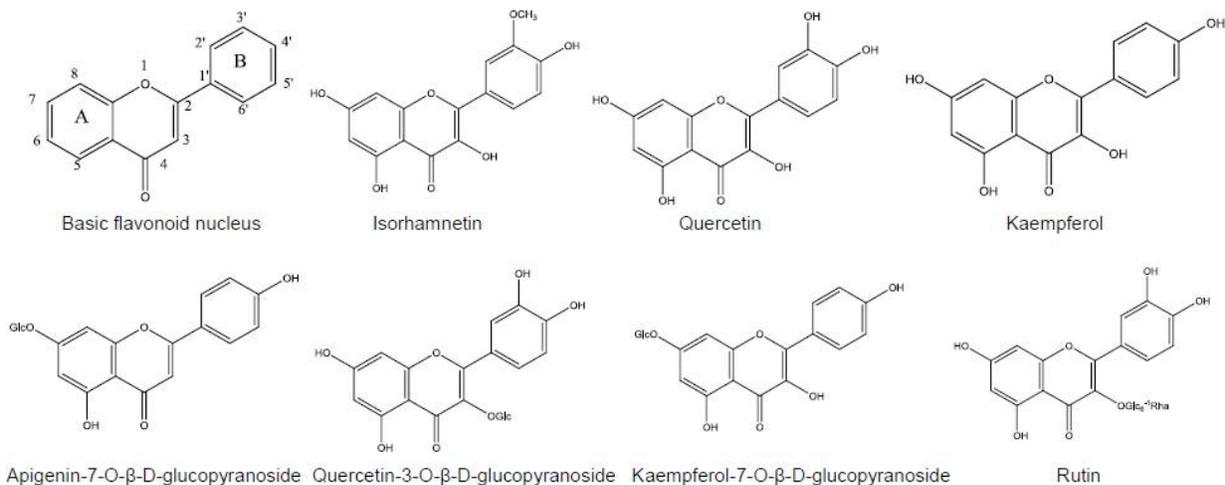


Figure 1: Structures of the flavonoids obtained from outer onion skins

Quercetin, in order to be used as corrosion inhibitor, is obtained from outer skins of onion by aqueous extraction method. Onion is a plant that can be found in everyday household kitchen. It is cheap, fairly abundant to be accessed, can be consumed, so it is safe and environmentally friendly. The extract of outer onion skins, can be used as corrosion inhibitor, because the compounds content on it, act in a synergic way. Also the inhibition efficiency, related with, the oxygen atoms in quercetin, that are electron rich and serves as a good adsorption site on the surface of the metal and ions present in water, which can cause corrosion. The inhibition efficiency (IE) of quercetin extracted from outer skins of onion was evaluated by weight loss method and potentiodynamic polarization measurements [5].

2. Materials and Methods

2.1 Preparation of onion skin's extract

The outer skins of onions first were dried in a dark place and were powdered in a grinder. The powder was extracted in boiled water for 1 hour. The extracted solution was then filtered and concentrated until the water evaporates, to half of the initial amount. The water extract in different concentration, was used to study the corrosion inhibition properties with both: weight loss method and electrochemical potentiodynamic measurements [13].

2.1.1 Weight Loss Method

Material under investigation is Aluminium. The samples used for the weight loss method are prepared from aluminium in cylindrical shape with diameter 5.5 ± 0.3 mm and high 40 ± 2 mm respectively as shown in Fig. 2. [6].



Figure 2: Preparation of samples for weight loss measurements.

The measurements were conducted in 1 M HCl solutions at the following concentrations of the extract: 0.25g/L, 0.5g/L, 0.75g/L and 1g/L (Table 1). All tests were obtained in deaerated solutions.

Table 1: The matrix for weight loss measurements.

No.	Blank	Concentration of extract (g/L)			
		0.25	0.50	0.75	1.00
1	+				
2	+	+			
3	+		+		
4	+			+	
5	+				+

By the weight loss method samples were placed in closed glasses container. Samples were exposed to aggressive environment (1M HCl) with and without the presence of the inhibitor for 48 hours. After 48 hours, the metal sample was removed from the container and its weight was recorded. Fig.3



Figure 3: The samples of aluminium

The corrosion rate () and the inhibition efficiency IE (%) was calculated from equations (1) and (2): () (1)

units Δm - the weight difference (mg), ρ - Density ($\rho = 7.86 \text{ g/cm}^3$),

A - Surface of the sample (cm^2),

t - Time of sample exposure (hours).

() (2)

Where, in corresponding unit:

V_0 and V are the corrosion rates of the specimen in acid solutions, without and with the addition of inhibitor respectively [8].

2.2.2 Electrochemical Potentiodynamic Measurements

The samples used for the potentiodynamic measurements are prepared from aluminium, in cylindrical shape with diameter 6 mm and 4 mm respectively and fixed inside a Teflon tube with epoxy resin as shown in Fig. 4 [7].

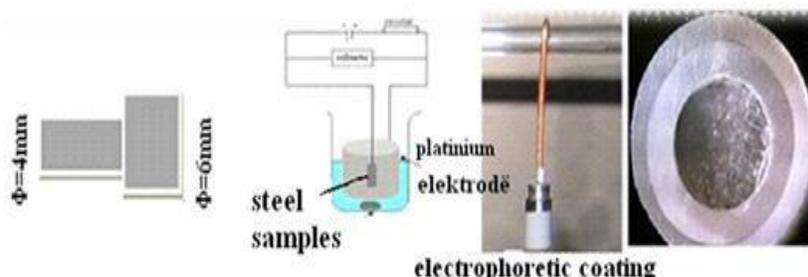


Figure 4: Preparation of samples for potentiodynamic polarization measurements.

The measurements were conducted in 1M HCl solutions at the following concentrations of extract: 0.25g/L, 0.5g/L, 0.75g/L and 1g/L, Table 2: All tests were obtained in deaerated solutions.

Table 2: The matrix for potentiodynamic polarization measurements.

No.	Blank	Concentration of extract (g/L)			
		0.25	0.50	0.75	1.00
1	+				
2	+	+			
3	+		+		
4	+			+	
5	+				+

Electrochemical potentiodynamic measurements were carried out in a three-electrode electrolysis cylindrical tempered glass cell. Aluminium, Hg/HgSO₄ electrode and platinum electrode were used as working, reference and auxiliary electrodes, respectively.

The polarisation curves were recorded with a Potentiostat/Galvanostat/TACUSSEL PJT 24-2 model at a scan rate of 6x10⁻³V/min [9, 10] The linear Tafel plots are utilized to provide information about the corrosion rate of aluminium and inhibitor efficiencies in 1 M HCl

solutions containing different concentration of extract. Corrosion current density was determined using the cutting point of Tafel extrapolation line and V_{corr} was calculated according to Faraday's law [9, 11] (3). () (3)

Wherein corresponding units:

M - Molar weight of the metal ($M = 56 \text{ g/mol}$), i_{corr} - is corrosion current density,

n - Number of electrons exchanged during metal dissolution ($n=2$), ρ - Density ($\rho = 7.86 \text{ g cm}^{-3}$),

K – Constant, which equals to 0.00327 if corrosion rate (V_{corr}) is calculated in [mm/year]. [8]

3. Results and Discussion

2.1 Weight Loss Measurements

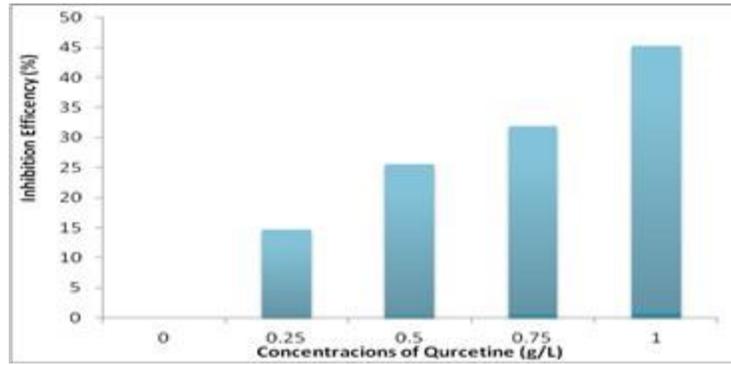
The weight loss method of monitoring corrosion rate is useful, because of its simple application and reliability. Table 4 shows the calculated values of corrosion rates obtained using Eq. (1) as well as inhibition efficiency evaluated using the expression given in Eq. (2).

Table 3, illustrates the metal weight loss in the presence of quercetin and it can be seen, that the weight loss has been reduced when concentration of extract, was increased gradually from 0.25 to 1 g/L. The reduction in metal weight loss for aluminium, demonstrating quercetin as an effective corrosion inhibitor [11]. The results show that the corrosion efficiencies in each acid media, increased with increased of inhibitor concentration and corrosion rates decreased with increased of inhibitor concentration [12].

The results are presented in form of corrosion rate (mm/year) and inhibition efficiency of different additives concentration against corrosion (Tab. 3). Also graphic 1. represents the relationship of inhibition efficiency (IE%) via concentration of extract (g/L).

Table 3: Corrosion rate and inhibition efficiency for aluminium in 1M HCl , with and without inhibitor (blank).

Weight loss measurements		
<i>Extract Concentration (g/L)</i>	<i>Corrosion rate (v) (mm/year)</i>	Inhibition Efficiency (IE%)
0 (blank)	0.4135	-
0.25	0.3525	14.5
0.50	0.2835	25.1
0.75	0.3090	31.1
1.0	0.2305	44.3



Graphic 1: Inhibition Efficiency of Quercetin via concentration of extract (by Weight loss method).

2.2 Electrochemical Measurements

The potentiodynamic polarization behavior of aluminium in 1M HCl solution is tested in the absence and in the presence of different concentrations (0.25g/L, 0.5g/L, 0.75g/L, 1g/L) of extract. The results taken by potentiodynamic measurements, are given as V_{corr} in millimeter per year, calculated using corrosion current density (i_{corr}). Corrosion current density is determined using the cutting point of Tafel extrapolation line. Potentiodynamic polarization curves are given in Fig. 5, 6, 7, 8, 9.

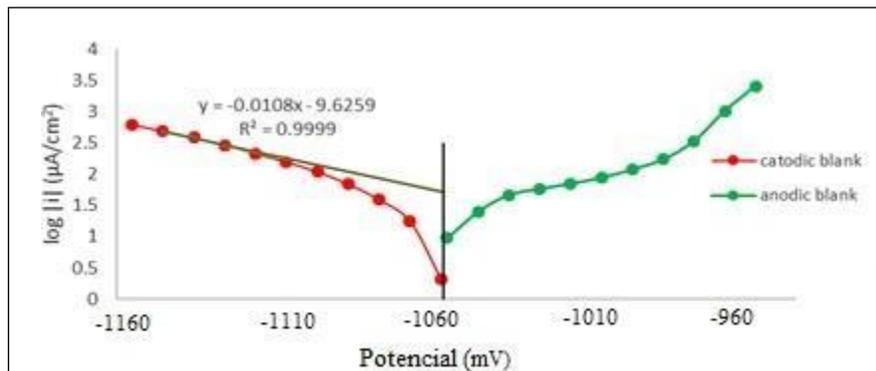


Figure 5: Potentiodynamic polarization curves for Aluminium deaerated in 1M HCl solution containing different concentration of quercetin.

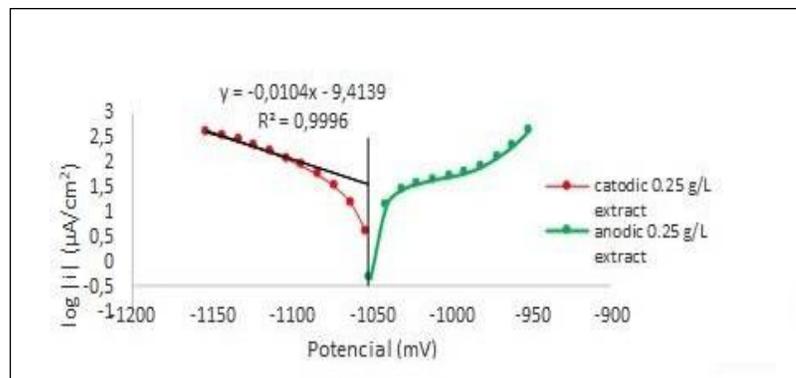


Figure 6: Potentiodynamic curves and Tafel extrapolations for aluminium in HCl 0.1 M, in presence of 0.25 g/L quercetin extract.

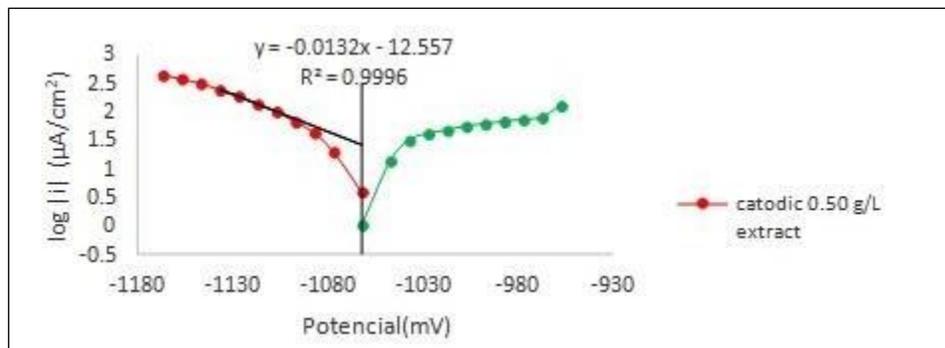


Figure 7: Potentiodynamic curves and Tafel extrapolations for aluminium in HCl 1M, in presence of 0.5 g/L quercetin extract.

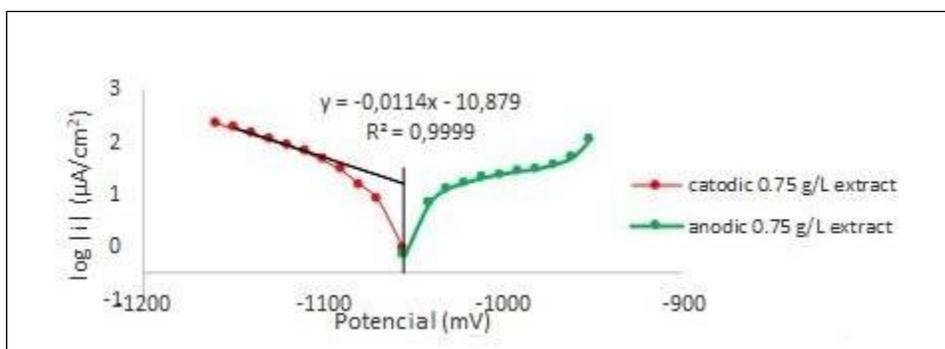


Figure 8: Potentiodynamic curves and Tafel extrapolations for aluminium in HCl 1M in presence of 0.75 g/L quercetin extract.

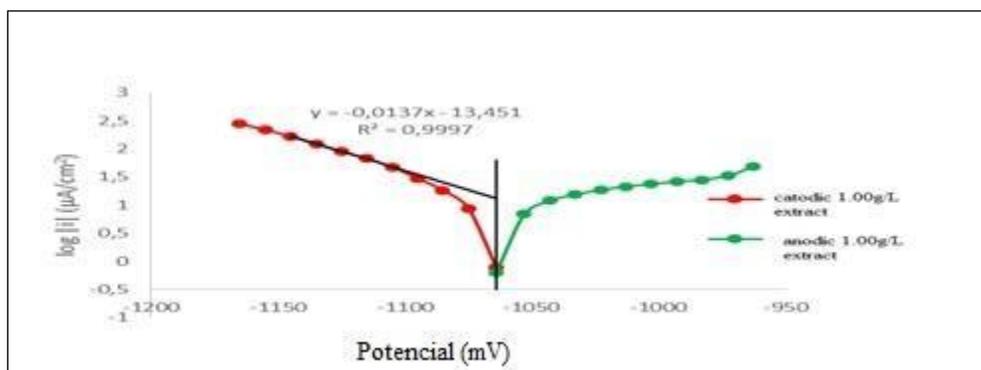
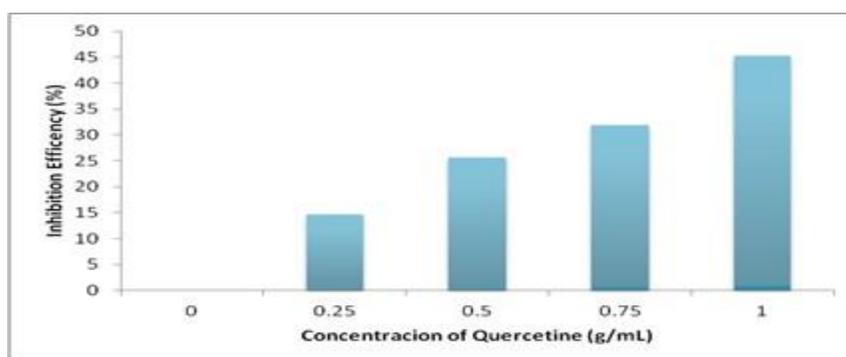


Figure 9: Potentiodynamic curves and Tafel extrapolations for aluminium in HCl 1M, in presence of 1 g/L quercetin extract.

Table 4: Corrosion potential, corrosion current density, corrosion rate and inhibition efficiency of extract of outer onions skin on aluminium in acid media

<i>Electrochemical measurements</i>				
Extract Concentration (g/L)	E _{corr} (mV)	i _{corr} (μA/cm ²)	Corrosion rate (v) (mm/year)	Inhibition Efficiency (IE%)
0 (blank)	-1054	51.62	0.56	-
0.25	-1052	37.27	0.41	26.8
0.50	-1062	26.00	0.28	50.0
0.75	-1055	15.45	0.17	69.6
1.0	-1064	13.03	0.14	75.0



Graphic 2: Inhibition efficiency of extract via concentration, by potentiodynamic polarization measurements.

In Tab. 4. are represented the corrosion potential value (mV), corrosion current density, corrosion rate and inhibition efficiency of extract of outer onions skin on aluminium in acid media.

The corrosion inhibition efficiency of extract for Aluminium in 1M HCl can be explained:

The extract of outer skin of onions contains quercetin, an electron rich site which allows the reaction of water molecules to take place. Consequently, instead of reacting with the metal ions found on the metal surface, the water molecules react with the electron found on quercetin, thus inhibiting the corrosion. This is essentially the most important property of an inhibitor should have.

Also, may be a protective film is formed on the metal surface through the interaction between the active site of metal surface and the lone pair of electrons of oxygen atom as aromatic ring.

The results for potentiodynamic polarization measurements show that the inhibition efficiencies of quercetin increased to reach an optimal concentration (Table 4).

4. Conclusions

Based on the experimental results, it has been proven that, quercetin can be used as a natural corrosion inhibitor.

It can be concluded that the objective of finding a natural substance that is environmentally friendly, economical and effective has been achieved.

- Quercetin is an efficient corrosion inhibitor on Aluminium surface in 1M HCl.
- For weight loss method, the inhibition efficiencies of quercetin, increased with increased of inhibitor concentration.
- For potentiodynamic polarization measurements, the inhibition efficiencies of quercetin increased to reach an optimal concentration.
- Quercetin exhibits the maximum protections in concentration 1 g/L for weight loss measurements and in 1g/L potentiodynamic polarization measurements.
- Inhibition efficiencies of quercetin for weight loss measurements is 44.3%.
- Inhibition efficiencies of quercetin for potentiodynamic polarization measurements is 75%.

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