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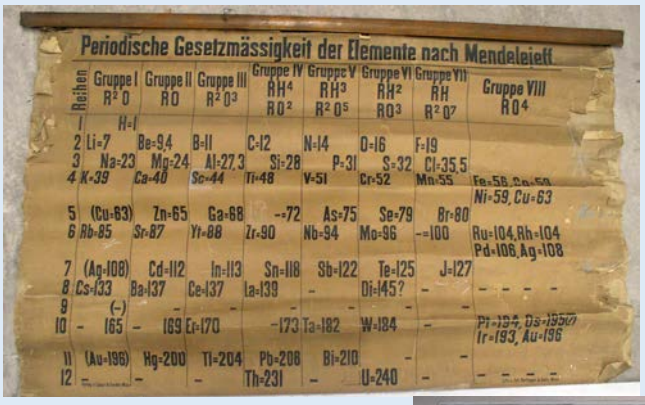
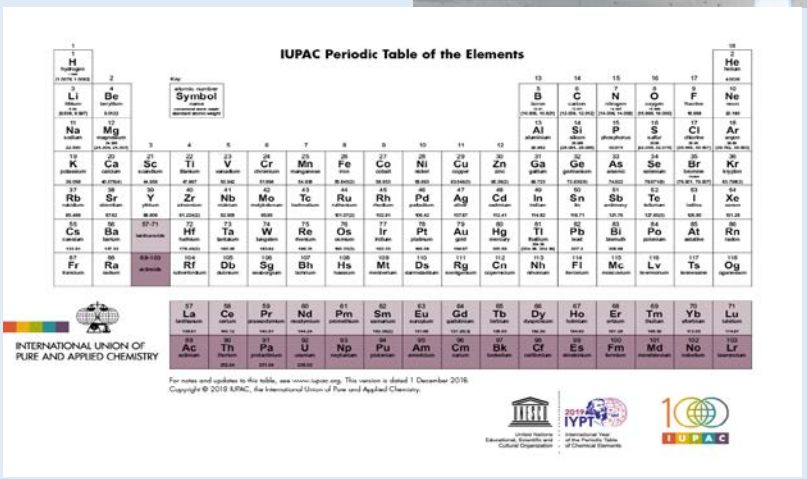


First periodic table- year 1869.

Periodic table in amphitheater of Faculty of Science made in 1962



Periodic table by IUPAC 2019 is 150 years of periodic table

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THE INTERNATIONAL YEAR OF THE PERIODIC TABLE

Advances of modern chemistry have in numerous ways transformed the lives of humans in ways once thought unimaginable. These developments once applied to the multitude of disciplines including industry, medicine, food production have led to a dramatic increase in population and in general quality of life and health of humanity as a whole. In an age of ever-increasing specialization and complexity, one can easily overlook that all of that advancement and experimentation boils down essential building blocks of matter, the atoms, and their classification as elements.

The general characterization of matter has existed from the ancient times in both philosophical and scientific manner, however, for centuries it was quite arbitrary and differed widely between different civilizations. In the European middle ages existed a fixation of many with the mostly mystical transmutation of matter, including the notable search for so-called “Philosopher's stone”. While these early experimentations where barely scientific in nature they did show that characteristics of materials can be manipulated and these have led to the discovery and classification of the first elements, even if though their properties where barely understood. As science progressed it became clear that all matter is made up from particles that were named atoms, with their first classification made by Antoine-Laurent de Lavoisierwhich and which were thought for a long time to be fundamental particles. With the accumulated knowledge of known elements relative atomic masses, in 1869 Dmitri Ivanovich Mendeleev published a table which is considered a first modern periodic table of elements in which known elements were arranged according to their properties with blank spaces being filled with further discoveries of new elements. This trend continues to this day with synthesis and characterization of short-lived highly unstable elements as well as different isotopes of known ones.

In the recognition of huge impact the creation and subsequent expansion of periodic table has had for the entire human civilization the year 2019, which is 150 years since the publication of Mendeleev’s periodic table, has been declared by the United Nations General Assembly and UNESCO as “The International Year of the Periodic Table “ with the aim of further promoting and supporting development of science and technology through the humanity.

Editors

Front page photos were taken from the internet in honour to celebrate 150 years of periodic table. Authors of this journal do not claim any rights on them.

https://phys.org/news/2019-01-world-oldest-periodic-table-st.html?fbclid=IwAR2uWizBRO85S3rnbayjOu8ijghuiGdBNU4X0iabFsiTtNw2QxUto5cyp_U
https://iupac.org/what-we-do/periodic-table-of-elements/

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Original Scientific Article

Inhibition of Iron Corrosion in Seawater Using Rosemary Extracts (*Rosmarinus officinalis* L.)

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Abstract: Due to a growing awareness of environmental protection, an interest in replacing toxic corrosion inhibitors with more environmentally acceptable alternatives is also growing. Chromates, as one of the best inhibitors, have been eliminated as technically viable inhibitors because of their high toxicity, and the use of polyphosphates has diminished as they disrupt the balance in the Plantae kingdom. The emphasis is on exploration and testing of organic compounds that can be obtained from plant material. Rosemary extracts (leaf and flower) have been shown to have inhibitory activity on iron corrosion in 3% NaCl and seawater. Corrosion rate values show that rosemary flower extracts are better inhibitors of corrosion than the leaf extracts and that the maximum inhibitory protection has not been achieved in the range of tested concentrations.

INTRODUCTION

Due to the development of industry, especially in the technological aspect, various types and forms of corrosion of metal and non-metallic materials are present. The reason for this is the rapid increase in the number of objects, devices, constructions, as well as the higher pollution intensity due to combustion of solid and liquid fuels (Kliškić, 2000).

In order to reduce the corrosion rate, except for the usual coatings, number of inhibitors are used. Inhibitors are substances which, when added to a corrosive environment, reduce corrosion rates to technologically acceptable rates (Pupovac, 2008). In order to meet the needs to preserve the environment, environmentally acceptable inhibitors are being used more often. This is particularly the case for extracts of various plants, which in their composition have compounds that can slow down the corrosion process (Radošević, 2012); (Pallav, 2014). Phenolic compounds have shown quite good protective properties, above all flavonoids. Some of them show the possibility of creating metal chelate complexes. (Radosevic, 2012-1); (Hogervorst Cvejić, 2016). Rosemary shows the ability to inhibit the corrosion of metals and metal alloys. Organic compounds containing heteroatoms such as sulfur, nitrogen or oxygen in their structure have shown to have a tendency to adsorb onto metal surfaces, creating a protective layer that can slow down the development of corrosion (Khan, 2015). Green corrosion inhibitors are biodegradable, do not contain heavy metals or other toxic components, so they are increasingly applied instead of chemicals, mainly toxic inhibitors.

The first step in the activation mechanism of these compounds is the adsorption on the metal surface. For the dissolution of the adsorption process it is necessary to have forces of attraction between the adsorbate and the metal surface. In adsorbed molecules, hemisorption can occur in the presence of heteroatoms (P, Se, S, N, O) with lone electron pairs, or aromatic rings. Decrease in the rate of cathodic or anodic or both reactions arises from the adsorption of inhibitors at the active corrosion points on the surface of the metal (Ahamad, 2010).

Rosemary

Rosemary (Rosmarinus officinalis L.) is a woody, perennial herb with fragrant, evergreen leaves and very small light-blue flowers. The leaves are very narrow, firm, leathery and 2-3 cm long. It is native to the Mediterranean region, where it grows on calcium rich soil, in dry climate and in salty sea air. The plants grow 1-3 m in height. Rosemary extracts include phenolic compounds (carnosol, carnosic acid, rosmanol), cinnamic acid derivatives (rosmarinic acids) and flavonoids (nepetin, nepitrin). The leaves also contain triterpenes such as ursolic acid (Velázquez-Gonzalez, 2014). Rosmarinic acid, carnosol and carnosic acid represent the most significant phenolic compounds of rosemary, with outstanding antioxidant properties (Erkan, 2008, Borrás-Linares, 2014). Carnosic acid has lipophilic properties, and rosmarinic acid is hydrophilic, so rosemary extracts can be used to prevent oxidation of both polar and non-polar nutritional products (Berdahl, 2015).

The sampled plant was collected in the area of Split, Croatia. The sampling was done on June 26th 2017.

Figure 1. Rosemary

EXPERIMENTAL

Preparation of samples

Reflux extraction

Dried rosemary leaves were ground into fine powder, weighed out 15 grams and immersed in 100 mL of solvent, i.e. redistilled water in a flask fitted to a condenser.

The solvent is heated until boiling. As the solvent evaporates, it enters the condenser where it condenses and returns to the flask. The extraction is carried out for one hour, followed by filtration through 110 mm filter paper - black ribbon and the resulting aqueous extract volumewas the total volume. The same procedure was carried out with rosemary flower.

Determination of total phenolic compounds content (Folin-Ciocalteau method)

In a series of 10 mL volumetric flasks, 200 µl of the sample of known concentrations was measured and dilute with about 6 mL of distilled water. 500 µL of Folin - Ciocalteu reagent was added, previously diluted with water in a ratio of 1:2. After 5-10 minutes, 1.5 mL of a 20% sodium carbonate solution was added and dilute the resulting mixture with water to 10 mL. Prepared samples are left 2h to stand at room temperature and their absorbance was measured at 765 nm. (Pavagada, 2010)

The total content of phenolic compounds is determined based on the calibration curve for gallic acid at the concentration range of 0.01-1.10 mg / mL.

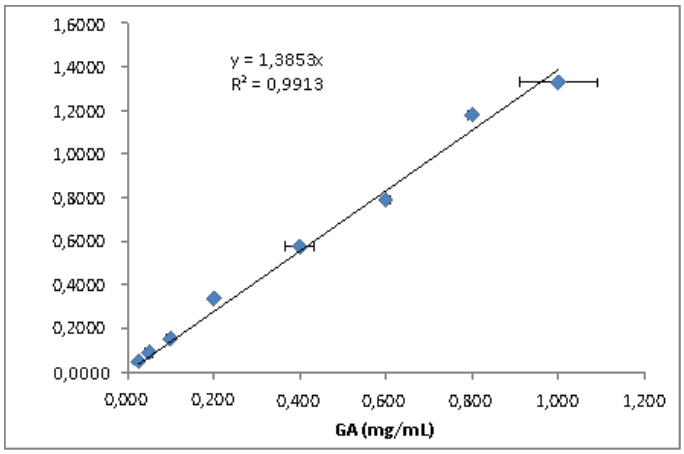

Figure 2. Calibration curve for the determination of total phenolic content

Table 1. Determination of concentration of phenolic compounds in the samples

Sample	γ (mg/mL)	V (mL)	γ work mg/mL)	A1	A2	A3	GAE work (mg/mL)	GAE work (mg/mL)	GAE work (mg/mL)	GAE (average)	GAE st.dev	%in sample	% in sample	%in sample	% in sample (average)	% in sample (st.dev.)	% recovery
Flower	105,11	0,10	35,04	0,1954	0,1866	0,1747	0,1411	0,1347	0,1261	0,2108	0,0899				0,0029	0,0002	7,90
	105,11	0,20	70,07	0,2849	0,301	0,3104	0,2057	0,2173	0,2241			0,0029	0,0031	0,0032			
	105,11	0,30	105,11	0,3934	0,3899	0,3923	0,2840	0,2815	0,2832			0,0027	0,0027	0,0027			
Leaf	1,68	0,10	0,56	0,4407	0,4521	0,4554	0,3181	0,3264	0,3287	0,4653	0,1613				0,3903	0,0415	10,62
	1,68	0,20	1,12	0,6646	0,6652	0,6629	0,4798	0,4802	0,4785			0,4283	0,4287	0,4273			
	1,68	0,30	1,68	0,8222	0,8202	0,8182	0,5935	0,5921	0,5906			0,3533	0,3524	0,3516			

It is necessary to determine the optimal concentrations of inhibitors because not every concentration is effective. Excessive or insufficient concentration of inhibitors can have an activating effect on corrosion of metals and the opposite effect of the desired one can be achieved. The inhibitor must be able to inhibit corrosion but also be present in the appropriate amount on the surface of the metal to demonstrate efficacy. Some inhibitors, if not present in sufficient concentration, may alter the corrosion distribution, but not the corrosion intensity. Therefore, it is necessary for each individual system to determine the concentration of the inhibitor that effectively protects against corrosion. Due to environmental and economic reasons, excessive consumption of inhibitors should be avoided. (Stupnišek - Lisac, 2007).

Preparation of iron tiles

The iron sampleswere sanded, first with fine sanding paper and rinsed with distilled water. Subsequently, they were immersed in a degreasing solution, heated to 90-95°C and held in it for 15-20 minutes. After degreasing, the samples are rinsed with warm, then cold water. The samples are then subjected to corrosion for 5 to 10 minutes. After corrosion and rinsing with cold water, the samples are briefly immersed in 3% H_2SO_4 solution. (Burovic, 2018).

Seawater was used for electrochemical testing. As a standard corrosive medium, 3% NaCl solution was used.

Work process

After adequately preparing the samples, iron plates were exposed to the corrosion media. For the linear polarisation and potentiodinamic experiments, PAR 263A potentiometer / galvanostat connected to the computer, with Power CV software was used. The measurements were performed in an electrochemical cell equipped with three electrodes (working, Ag/AgCl as reference and Pt as auxiliary electrode) at 25°C. The sample was polished using the Al2O3 powder. After coating the working electrode with teflon tape, the plate was immersed in the activating solution [V(H_2SO_4, conc): V(H_2O_2, conc) = 1:1) for one minute and then rinsed with distilled water. 40 mL of corrosive medium is added to the electrochemical cell and then the electrode were submerged in the solution. The linear polarization measurements were performed ± 25 mV from the corrosion potential Ecorr, which was determined by a potentiodynamic method in a wider range of potentials at a scan rate of 0,166 mV/s (Korać, 2010). The reference diagrams were recorded ± 250 mV in relation to the mentioned potential.

RESULTS AND DISCUSSION

Iron plates without inhibitors

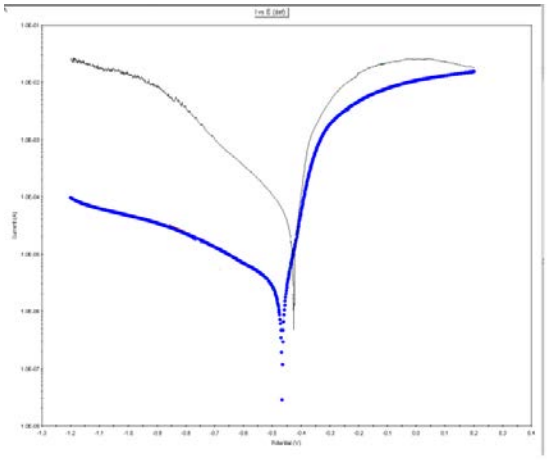

Figure 3. Tafel diagrams for the iron plate in 3% NaCl solution; SW wihout inhibitors

From the voltamogram it is noticeable that there is a certain passivation in the anode direction that is characteristic of the iron sample used for testing. Such behavior was repeated on all other test results.

- Iron plates in 3% NaCl solutions, with rosemary leaf extracts of various concentrations

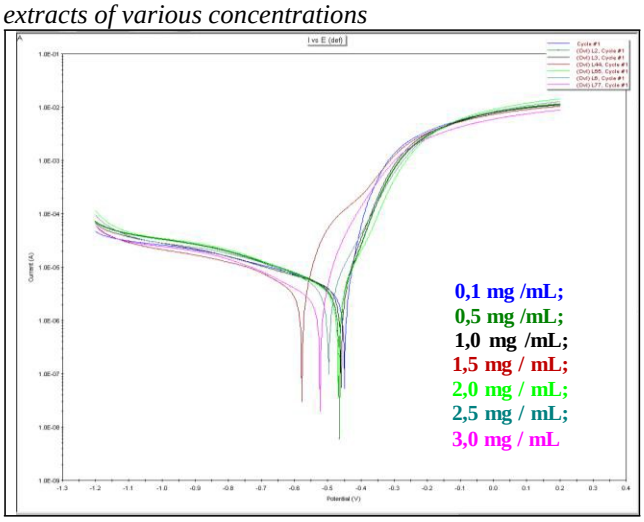

Figure 4. Tafel diagram, inhibitory activity of rosemary leaf extracts of various concentrations in 3% NaCl solution

The same phenomenon of passivation is repeated in the application of inhibitors, but there is no longer a scattering of results as in the measurement with no used extracts. The reason for this can be the formation of a protective layer of metallocomplex that equalizes the surface and makes the surface behave uniformly in the action of the corrosion medium.

- Iron plates in seawater, with rosemary leaf extracts of various concentrations

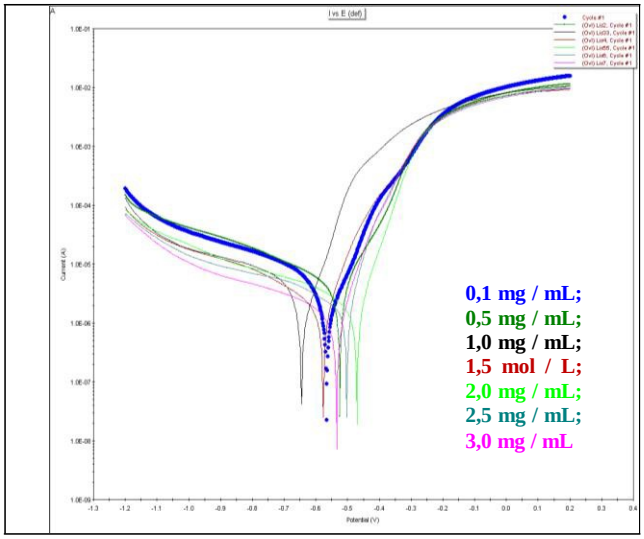

Figure 5. Tafel diagram, inhibitory activity of rosemary leaf extracts of various concentrations in seawater

The regularity is repeated in the seawater. More detailed parameters of the behavior of iron in seawater are given by corrosion parameters obtained from these voltamograms.

- Iron plates in 3% NaCl solution, with rosemary flower extracts of various concentrations

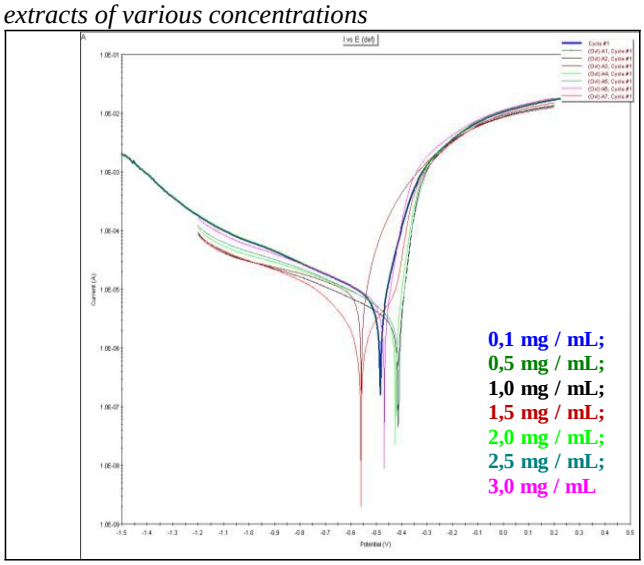

Figure 6. Tafel diagram, inhibitory activity of rosemary flower extracts of various concentrations in 3% NaCl solution

The rosemary flower extract behaves in a very similar manner as the leaf extract. By increasing the concentration of the extract, the correct displacement of Tafel curves can be noticed.

- Iron plates in seawater, with rosemary flower extracts of various concentrations

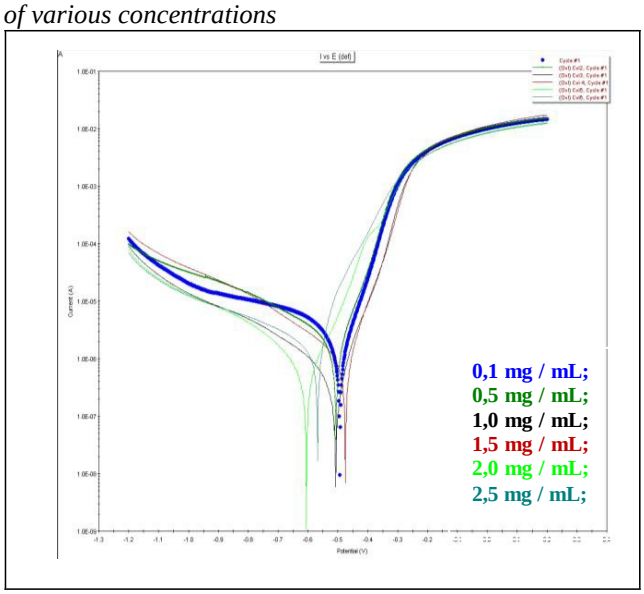

Figure 7. Tafel diagram, inhibitory activity of rosemary flower extracts of various concentrations in seawater

Rosemary flower extracts in seawater have a similar corrosion profile as previous cases.

By comparing all the results of the measurements, it can be seen which conditions of corrosion and concentration of individual leaf and flower extracts provide suitable combinations for the most efficient protection of iron with environmentally acceptable inhibitors. It is necessary to bear in mind the stability and biodegradability of the metallocomplex, and from the economic point of view the amount of inhibitors that will show the optimal protection role.

Corrosion potential is derived from Tafel diagrams (Figures 3 to 7). Using the method of extrapolation of the direction of the cathodic and anodic curves, Tafel's constants β_A and β_K were determined Corrosion current and corrosion rate values will to be shown in the following tables.

Table 2. The measurement results for iron plates in 3% NaCl solution, without and in the presence of rosemary leaf extract

mg/mL	E_{corr} [mV]	β_A [mV/dec]	β_K [mV/dec]	Rp [mV/μA]	i [μA]/cm^2]	v [mm/y]
0	-466	0,037175	0,073099	0,000132	3,40999	0,046509
0,1	-450	0,037051	0,051414	0,000148	3,135528	0,045004
0,5	-465	0,055804	0,214592	0,000169	3,061832	0,048191
1	-459	0,064103	0,058789	0,000181	2,981226	0,041393
1,5	-589	0,041806	0,086881	0,0002055	2,90949	0,037791
2	-461	0,048685	0,136503	0,000253	2,78408	0,034914
2,5	-497	0,084674	0,196155	0,000251	2,788049	0,035523
3	-516	0,089206	0,515198	0,000267	2,668114	0,031289

Table 3. The measurement results for iron plates in seawater, without and in the presence of rosemary leaf extract

mg/mL	E_{corr} [mV]	β_A [mV/dec]	β_K [mV/dec]	Rp [mV/μA]	i [μA]/cm^2]	v [mm/y]
0	-420	0,042662	0,115075	6,11E-05	2,826804	0,03468
0,1	-565	0,088968	0,131822	8,46E-05	2,95382	0,032876
0,5	-524	0,081566	0,261917	0,000101	2,764258	0,034073
1	-521	0,096061	0,213129	1,29E-04	2,694553	0,031353
1,5	-576	0,095602	0,695894	1,35E-04	2,368884	0,027736
2	-549	0,082034	0,569152	1,22E-04	2,347532	0,026827
2,5	-502	0,072254	0,263158	1,50E-04	2,25243	0,023714
3	-534	0,072993	0,348068	1,53E-04	2,24557	0,021634

Table 4. The measurement results for iron plates in 3% NaCl, without and in the presence of rosemary flower extract

mg/mL	E_{corr} [mV]	β_A [mV/dec]	β_K [mV/dec]	Rp [mV/μA]	i [μA]/cm^2]	v [mm/y]
0	-466	0,037175	0,073099	0,000132	3,40999	0,046509
0,1	-411	0,028498	0,083472	0,000119	2,223813	0,028696
0,5	-414	0,03023	0,163934	0,000196	2,178352	0,025505
1	-558	0,036689	0,087336	0,000225	2,061973	0,024926
1,5	-424	0,031437	0,049188	0,000237	1,925288	0,0222
2	-410	0,031368	0,046598	0,000257	1,890771	0,02448
2,5	-468	0,041528	0,048567	0,000271	1,608102	0,020245
3	-560	0,041391	0,07446	0,000314	1,353771	0,019559

Table 5. The measurement results for iron plates in seawater, without and in the presence of rosemary flower extract

mg/mL	E_{corr} [mV]	β_A [mV/dec]	β_K [mV/dec]	Rp [mV/μA]	i [μA]/cm^2]	v [mm/y]
0	-420	0,042662	0,115075	6,11E-05	2,826804	0,03468
0,1	-494	0,060024	0,087184	0,000066	2,020109	0,019944
0,5	-506	0,0815	0,36062	6,73E-05	1,944281	0,017764
1	-508	0,059137	0,096974	7,70E-05	1,923125	0,012612
1,5	-475	0,072202	0,240906	8,13E-05	1,907821	0,011332
2	-605	0,081301	0,128469	9,16E-05	1,872797	0,010536
2,5	-568	0,079239	0,29967	1,03E-04	1,312477	0,009392
3	-590	0,106304	0,329815	0,000107	1,2733	0,00707

Data from Table 2 to Table 5 are presented in a Figure 8.

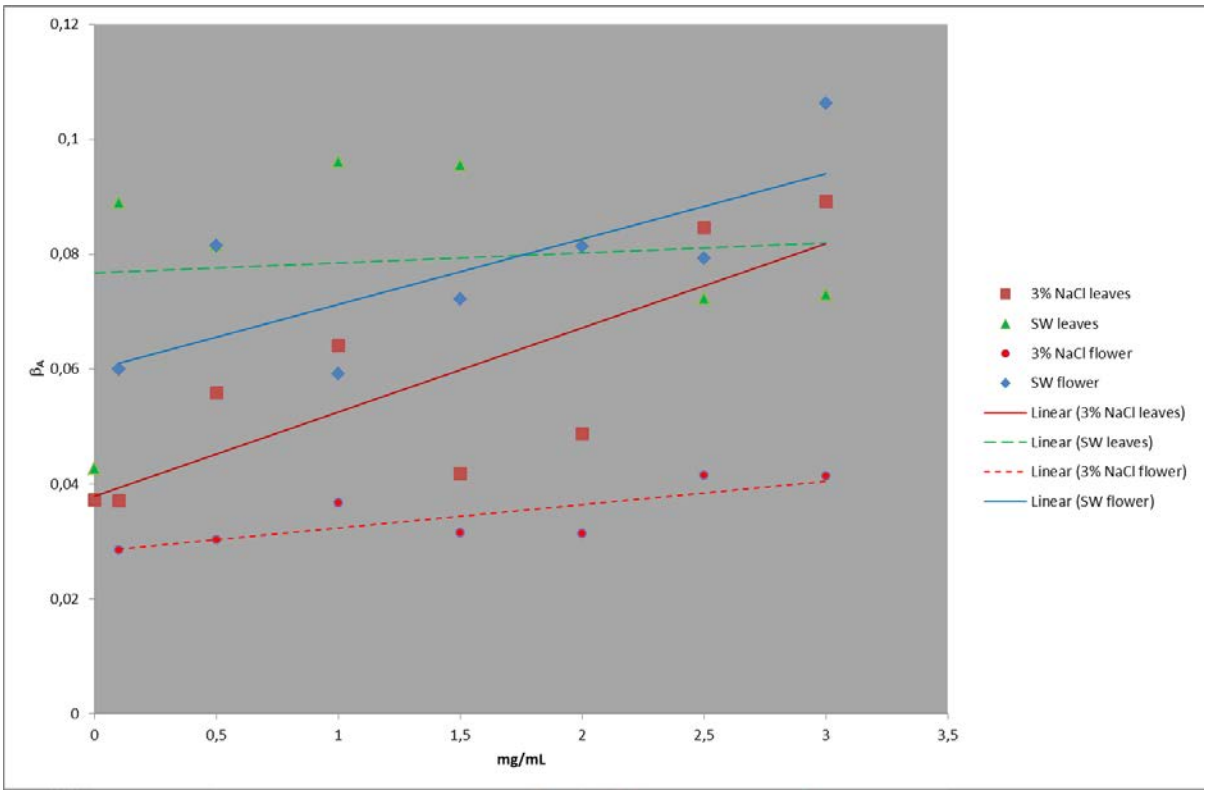

Figure 8. Dependence of Tafel's anodic slope of different concentrations of inhibitors in various corrosion media

From Figure 8 it can be concluded that the value of Tafel's anodic slope increases with the change of concentrations of extracts in both corrosion media as well as in both extracts. It can be noted that inhibitors derived from plant extracts affect the anodic reaction and alter it. A slight effect on the anodic reaction is shown. In these measurements, when a significant change in the rate of corrosion occurs, it appears that the inhibitor also affects the cathodic reaction in the given system.

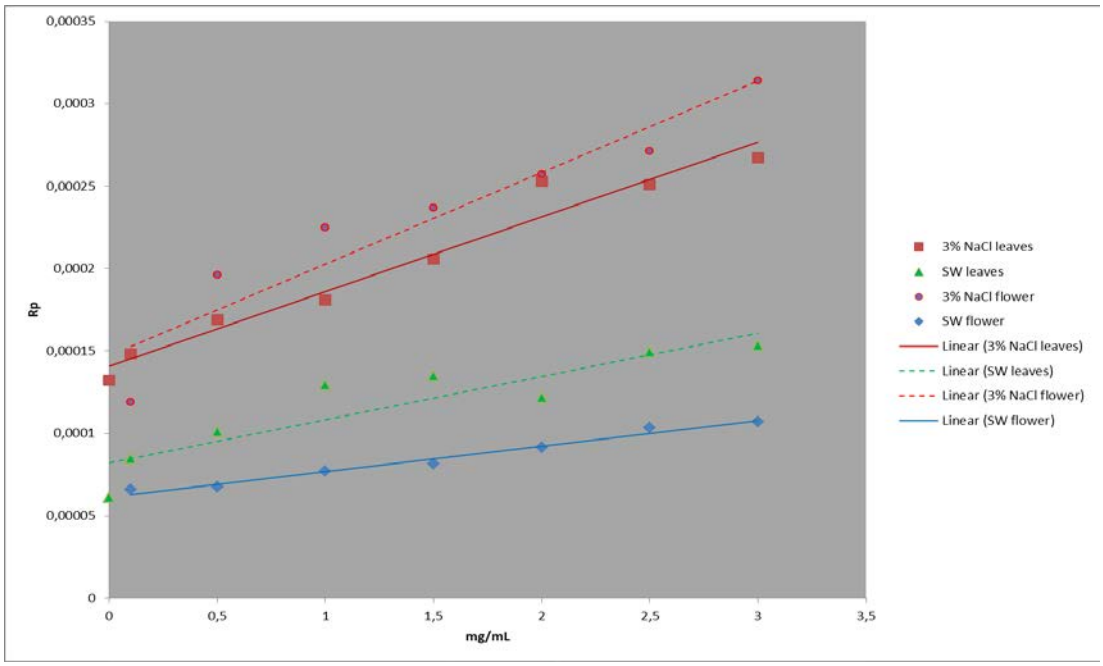

Figure 9. Dependence of polarization resistance of different inhibitor concentrations in various corrosive media

From Figure 9 it can be concluded that the values of polarization resistances are higher in the leaf extracts than in flower extracts. Polarization resistance values show higher value for samples

that have better protection.. Based on these values of Rp, it can be assumed that the creation of a protective layer on the surface of the metal that changes the electrical conductivity is present. Due to the structure of this film, it can also be said that there is a less conductive form which also contains organic components that produce relatively stable complexes with the metal.

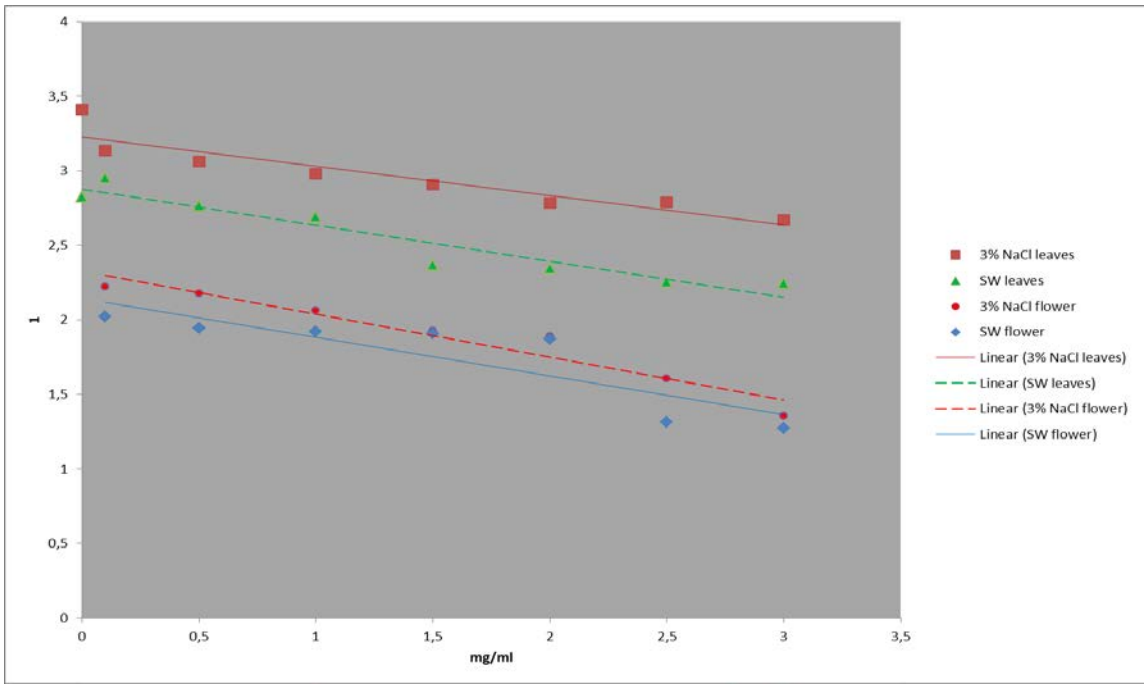

Figure 10. Dependence of corrosion current of different inhibitor concentrations in various corrosive media

Corrosion current can also be used as an indicator of inhibitory activity. The lower the corrosion current value, the more effective the inhibitor is. Figure 10 shows that flower extracts are more effective than leaf extracts. Also the marine environment is less aggressive than the 3% NaCl solution. It can be concluded that some seawater compounds further inhibit iron corrosion.

It is shown that, due to the action of the protective film, the increase in the concentration of the inhibitor decreases the corrosion current because it reduces the conductivity and accessibility of the metal in the structure to the action of the corrosion environment.

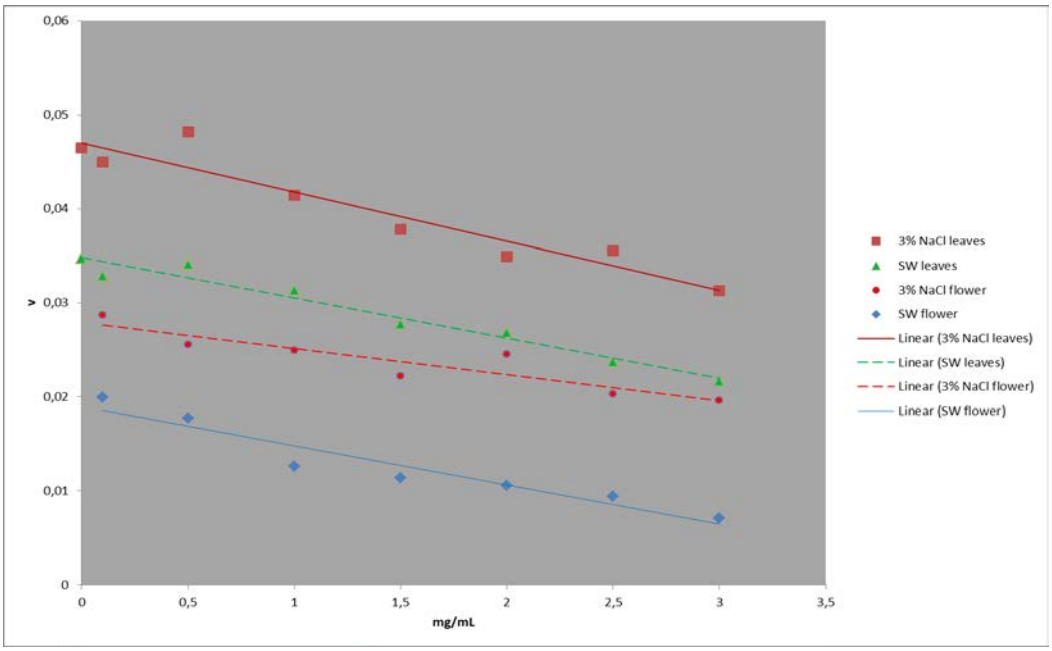

Figure 11. Dependence of corrosion rate of different inhibitor concentrations in various corrosive media

As corrosion currents demonstrate the efficacy of inhibitors, the corrosion rate is also a measure of protective activity. The lower the rate, the greater the efficiency of the inhibitor.

From Figure 11 it is concluded that when the flower extract is more efficient, the corrosion rate is lower, and that 3% NaCl solution is less suitable for the formation of the metal complex layer on the surface of the metal. It is assumed that the resulting metal complexes become passivated on the surface and that it is less soluble than in 3% NaCl solution.

Based on the experiences observed, it was expected that some concentrations would significantly alter the mechanism of action of inhibitors that would be reflected in a noticeable change in the rate of corrosion. It was not seen here. The reason for this may be that the entire surface of the metal is equally covered by a protective layer of metallocomplex that would more effectively protect the metal from the action of the corrosion environment. Due to the complexity of seawater composition, better coverage of metals and lower corrosion rate were observed.

CONCLUSIONS

Based on the results of the research, general conclusions can be drawn.

- Based on the concentrations and calibration curves of gallic acid, the content of phenolic compounds in leaf extracts and rosemary blossoms can be determined;
- Rosemary (leaf and flower) extracts can be used as an iron corrosion inhibitor in seawater;
- Rosemary flower extract was shown to be a better inhibitor than leaf extract.

From the values of Rp, v_{corr} and Tafel's anodic slope it can also be concluded that:

- the value of Tafel's anodic slope increases with the change of concentrations of extracts in both the corrosion media, as well as in both extracts;
- the polarization resistance values are higher in the leaf extract than in the flower extract. Polarization resistance shows higher value for samples that have better protection;
- Flower extracts are more effective inhibitors than leaf extracts. Also, the marine environment is less aggressive than the 3% NaCl solution. It can be concluded that some seawater compounds further inhibit iron corrosion;
- the flower extract is more efficient, the corrosion rate is lower, and that 3% NaCl solution is less suitable for the formation of the metal complex layer on the surface of the metal;
- It is assumed that the resulting metal complexes become passivated on the surface and that it is less soluble than in 3% NaCl solution;
- There was no stagnation in one of the parameters, to conclude that there was no complete overcoating of the surface with the protective layer and that this protective effect could be improved.

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Summary/Sažetak

Zbog porasta svijesti o očuvanju životne sredine, poraslo je interesovanje za zamjenom toksičnih inhibitora korozije ekološki prihvatljivijim. Hromati, kao jedni od najboljih inhibitora, zbog izražene toksičnosti, uklonjeni su kao tehnički primjenjivi inhibitori, a smanjena je upotreba i polifosfata jer remete ravnotežu u biljnom svijetu. Akcenat je dat ka istraživanja i ispitivanju organskih spojeva koji se mogu dobiti iz biljnog materijala. Pokazalo se da ekstrakti ruzmarina (iz lista i cvijeta) imaju inhibitorsko djelovanje na koroziju željeza u 3% rastvoru NaCl i morskoj vodi. Vrijednosti brzine korozije pokazuju da su ekstrakti cvijeta ruzmarina bolji inhibitori korozije od ekstrakta lista, i da nije dostignut maksimum inhibitorske zaštite u rasponu ispitivanih koncentracija.

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Curcumin: Phytochemical Therapy in the Treatment of Hyperlipidemia

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Abstract: In modern world, hyperlipidemia is the most common disorder mainly caused by lifestyle habits and the major cause of cardiovascular, coronary and atherosclerotic changes. Such disorder is characterized by abnormally elevated levels of any or all lipids or lipoproteins in the blood. A wide range of drugs are available for the treatment of hyperlipidemia, class of antihyperlipidemic drugs, but such drug-therapies are carried out with presence of various side effects. In the last decades, different *in vitro* and *in vivo* research have been conducted to confirm the therapeutic effects of various phytochemical agents that overcome the side effects caused by synthetic drugs. According to Ayurvedic recommendations and experimental studies, numerous phytochemical agents have been reported to possess different antihyperlipidemic properties. One of the most studied phytochemical agent - curcumin, herbal polyphenol and active ingredient which can be extracted from the powder rhizome of the plant *Curcuma longa*, has been reported to possess a wide range of pharmacological properties such as antimicrobial, antioxidative, antiinflammatory and anticancer property. Recent studies also suggests curcumin as potential lipid lowering candidate in treatment of hyperlipidemia. The aim of this review is to present and discuss phytochemistry, molecular mechanism of hypolipidemic activity of curcumin, demonstrating its importance as potential therapy for the treatment of hyperlipidemia.

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INTRODUCTION

Cardiovascular diseases are defined as “modern massive illnesses” due to their leading role in mortality worldwide. It is assumed that cardiovascular diseases will be the leading cause of mortality and disabilities by the year 2020 (Jorgensen *et al*., 2013). There are many risk factors associated with cardiovascular disorders such as age, sex, hypertension, hyperlipidemia, type 2 diabetes mellitus and metabolic syndrome.

Hyperlipidemia is the major and most common cause of cardiovascular disorders and it is described as a disorder of abnormal levels of lipids and lipoproteins in the blood (Durrington, 2003). Several studies have shown that low concentrations of low-density lipoprotein cholesterol and triglycerides are associated with low risk of cardiovascular disorders (Srikanth and Deedwania, 2016; Bhatt *et al*., 2010; Stone *et al.*, 2013). Therefore, appropriate and on-time treatment of hyperlipidemia is the most important prevention of cardiovascular disorders. A wide range of drugs, a class of antihyperlipidemic drugs, is available for the treatment of hyperlipidemia.

Modern pharmaceutical science has classified antihyperlipidemic drugs into five major classes that include statins, fibric acid derivates, bile acid binding resins, nicotinic acid derivatives, and drugs that inhibit cholesterol absorption (Dipiro *et al.*, 2008). The benefits of all those classes of drugs are well documented. There are efficient and well-tolerated drugs, but however, they possess various side effects. For instance, statins can cause myopathy, rhabdomyolysis and increased serum transaminase, and such substances can also cause kidney damage (Bellosta, Paoletti and Corsini, 2004). Due to such side effects, pharmaceutical industry seeks towards producing drugs with less side effects and discovering natural substances as alternatives to existing therapies.

Phytotherapy is a growing area of complementary medicine and natural products, phytochemicals are

becoming more popular than synthetic drugs due to their small range of side effects and low negative impact on the environment (Magi and Sahk, 2003). Phytochemicals, also referred as phytonutrients, are mainly found in vegetables, fruits, spices, nuts, herbs and seeds and are classified according to their chemical structures. The total number of phytochemicals is still unknown, so far the number of identified phytochemicals is about 10,000 (Zhang *et al.*, 2015). They occur in low concentration and demonstrate wide range of pharmacological activity (Watzl and Leitzman, 2012). For some of them, pharmacological studies have proven their impact in the modulation of cholesterol synthesis and absorption of lipids, while others have been shown to reduce blood pressure and inflammation processes (Yin *et al.*, 2016).

Evidence from epidemiological studies indicates a positive correlation between reduction in the incidence of cardiovascular disorders and consumptions of plant-based food rich with phytochemicals (Dauchet *et al.*, 2005). Recent findings show that phytochemicals possessing hypolipidemic properties may be the first choice in the treatment and prevention of hyperlipidemia (Sikder *et al.*, 2014). One of the most studied phytochemicals in the past decades is curcumin - natural product that can be extracted from the rhizome of the plant turmeric, *Curcuma longa* L. (Zingiberaceae). Boiled and dried plant's rhizome is mainly used as medicinal agent with a very specific yellow colour of the powder. In addition to its medical properties and because of such colour, powder is very often used as a coloring agents. The main components of turmeric are curcumin (60%), desmethoxycurcumin, monodemethoxycurcumin, bisdemethoxycurcumin and cyclocurcumin. The main bioactive ingredient is curcumin with a wide range of pharmacological effects such as cell cycle arest, induction of apoptosis, and anti-inflammatory activity.

This phytochemical has been used as a traditional medicinal agent in Ayurvedic medicine for ~6000 years and its pharmacokinetic, pharmacodynamic and clinical pharmacological properties have been extensively studied (Aggarwal, Kumar and Bharti, 2003). Different scientific findings indicate that curcumin possesses a wide range of pharmacological properties. These studies indicated that curcumin acts as an antioxidant, anti-inflammatory and anti-atherosclerotic; inhibits scarring, cataract, and gallstone formation, promotes wound healing and muscle regeneration; prevents liver injuries and kidney toxicity; and exerts medicinal benefits against cardiovascular diseases, diabetes, Alzheimer's and multiple sclerosis. Additional studies on cardioprotective and anticancer properties of curcumin have been performed (Beevers and Huand, 2011). Srivastava *et al.* reported on the first evidences of curcumin against cardiovascular disorders. They studied the effects of curcumin on the induction of myocardial ischemia by the ligation of the left coronary artery. Their findings demonstrated promising results in the protection and prevention of the ischemia-induced elevation of malonaldialdehyde and lactate dehydrogenase release (Srivastava *et al.*, 1985). Numerous phytochemical candidates have been studied for the treatment of hyperlipidemia and prevention of cardiovascular diseases, but curcumin has demonstrated the highest antihyperlipidemic effects based on preclinical and clinical trials conducted with promising results.

Chemistry of Curcumin

Curcumin or diferuloylmethane is a symmetric, hydrophobic natural product with IUPAC name (1*E*,6*E*)-1,7-bis(4-hydroxy-3-methoxyphenyl) hepta-1,6-diene-3,5-dione. It was isolated in 1815 and its chemical configuration was described in 1973 by Whiting and Roughley. The chemical structure of curcumin is shown in Figure 1. It consists of two phenolic rings, each substituted with a methoxy ether functionality in the *ortho*-position. The two phenolic rings are connected via an aliphatic unsaturated heptane linker in *para*-position that also contains α, β diketone functionality on carbon-3 and -5.

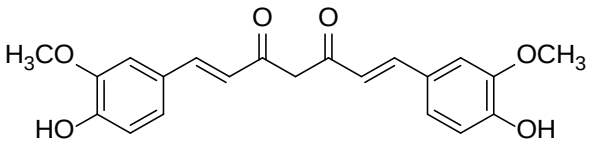

Figure 1: Chemical structure of curcumin.

Curcumin is an orange-yellow crystalline substance that is soluble in ketone, ethanol, dimethylsulfoxide, alkalis, acetic acid and chloroform and is insoluble in water. The absorption in the visible region of curcumin ranges from a maximum 410 to 430 nm, while the UV region has maximum absorption at 265 nm. Different studies have described tautomerization of curcumin and obtained results have demonstrated the ability of diketone functionality to undergo reversible tautomerization between enol and keto forms in pH-dependent manners (Payton *et al.*, 2007).

It has been showed that curcumin undergoes degradation in aqueous-organic solutions and that such degradation increases with increasing pH, thus limiting its use. However, when attached to lipids, surfactants, albumins, polymers and other macromolecular systems its degradations decreases (Priyadarsini, 2009).

The biosynthetic route of curcumin has proven to be very difficult to determine and there are two proposed mechanisms for curcumin biosynthesis. The first mechanism is explained as a chain reaction between cinnamic acid and 5 malonyl-CoA molecules that arylated into curcumin. While the second mechanism involves two cinammate units being bonded together by malonyl-CoA (Kita *et al*, 2008).

Molecular Mechanisms Of Curcumin

Since curcumin exhibits a wide range of pharmacological effects, it was very difficult and challenging for researchers to discover the primary molecular targets of the compound and mechanisms of action. Evidence indicates that curcumin affects multiple molecular targets and highly complex molecular mechanisms that depend on its capacity of interacting and regulating these targets.

So far, it has been described that curcumin targets transcription factors, kinases, inflammatory cytokines, enzymes, adhesion molecule, proteases, cell surface receptors, transporters and apoptotic factors (Aggarwal,

Kumar and Bharti, 2003). A variety of curcumin molecular targets is presented in Figure 2.

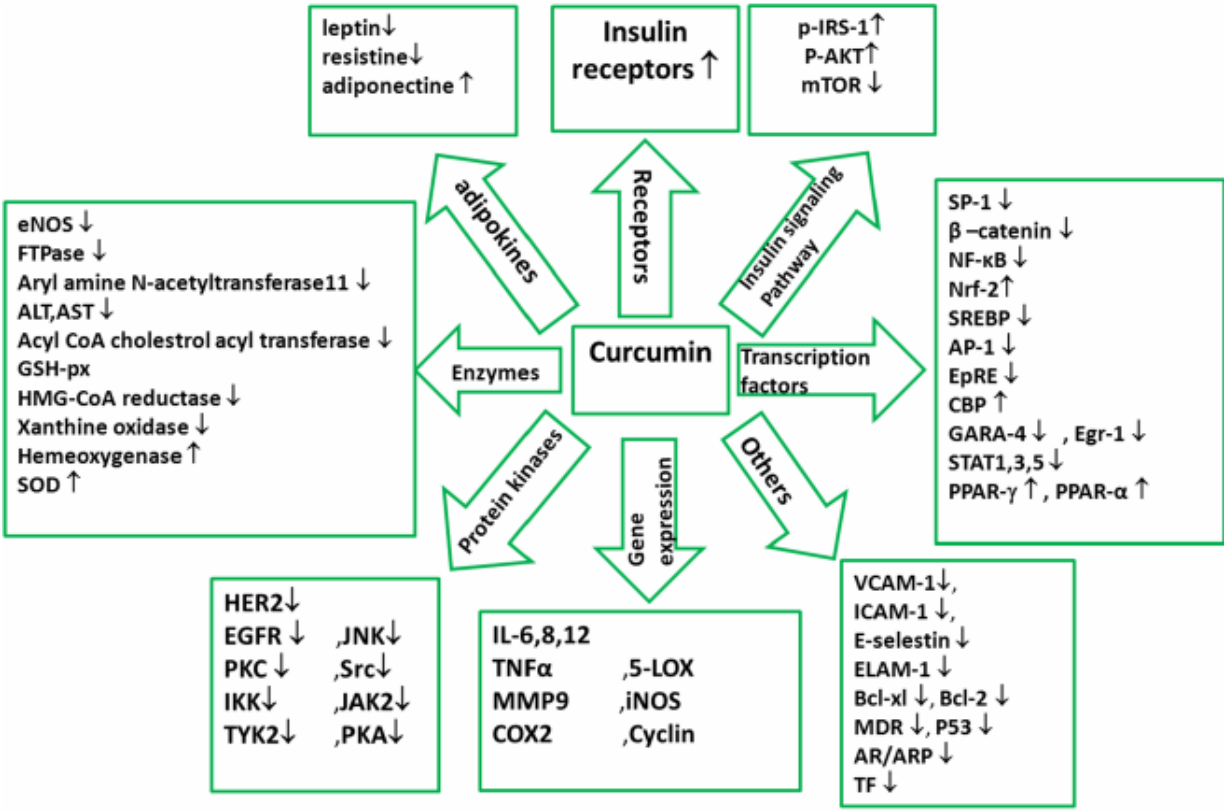

Figure 2: Different molecular targets effected by curcumin.

Transcription factors play a significant role in many metabolic processes and they can be induced or inhibited by many substances. Factors such as nuclear factor-κB (NF-κB), activated protein-1 (AP-1), signal transducer and activator of transcription (STAT) proteins, hypoxia-inducible factor-1 (HIF-1), Notch-1, early growth response-1 (Egr-1) and β-catenin are being inhibited by curcumin via different molecular mechanisms.

On the other hand, transcription factors such as peroxisome proliferator-activated receptor-gamma (PPAR-γ), NF-E2-related factor (Nrf2), aryl hydrocarbon receptor (AhR), electrophile response element (EpRE) and aryl hydrocarbon receptor (AhR) are affected and activated by curcumin. Many of these transcription factors are involved in very important life processes such as cell survival, cell proliferation, inflammation and angiogenesis. As curcumin targets many of those factors, it has been suggested that all those processes can be modulated by its influence (Sharma, Gescher and Steward, 2005; Shishodia, Sethi and Aggarwal, 2005).

Besides the transcription factors, a significant role in the normal process of growth and differentiation is given to growth factors. Different growth factors are described as one of the molecular targets of curcumin that can be modulated and activated by curcumin, thereby exhibiting antiproliferative, anti-invasive an antiangiogenic effects.

It has been shown that curcumin inhibits lung adenocarcinoma PC-14 and pancreatic adenocarcinoma p34 cells proliferation by modulating extracellular receptor kinase (Soung and Chung, 2011).

Curcumin also has the ability of scavenging a variety of reactive oxygen species (ROS) that includes superoxide anion, singlet oxygen, nitric oxide and peroxynitrite. This ability provides curcumin a significant role in protection of lipids and DNA from oxidative degradation. All three forms of curcumin possess this ability, but the pure curcumin is a more potent scavenger than demethoxycurcumin or bisdemethoxycurcumin (Subramanian *et al.*, 1994; Kunchandy and Rao, 1990).

Evidence indicates that curcumin is involved in the lipid peroxidation process, which is the main trigger for the development of many cardiovascular disorders. Different *in vivo* and *ex vivo* studies confirmed the ability of curcumin to lower plasma lipid peroxides and reduce LDL vulnerability to the oxidation process. Further studies have also demonstrated antithrombotic effects of curcumin (Rao, 1994).

Molecular Mechanisms Of Hypolipidemic Activity Of Curcumin

In recent years, there has been a growing interest in the potential pharmacological effects of curcumin in the treatment of hyperlipidemia and prevention of cardiovascular diseases. It has been demonstrated that curcumin can be as effective in reducing total cholesterol and triglycerides as statins, drugs prescribed to patients with hyperlipidemia and atherosclerotic disorders.

Several *in vivo* studies were conducted on different animal models and majority of evidence demonstrate that the lipid-lowering potential of curcumin is due to the ability of curcumin to decrease the circulatory levels of lipid peroxidase, total serum cholesterol (TC), and increase the circulating levels of high density lipoprotein-cholesterol (HDL-C) (Fan *et al.*, 2006).

Animal study conducted on high-fat diet-fed hamsters has demonstrated that the feeding with curcumin leads to a significant reduction of hepatic cholesterol and

triglycerides (Um *et al.*, 2013). Therefore, it was assumed that curcumin interacts with molecular targets associated with the intestinal absorption of cholesterol and free fatty acids metabolism. Due to such evidence, it can be concluded that orally applied curcumin actually causes ameliorating impact on lipid profiles in subjects with hyperlipidemia.

Zhao *et al.* described that molecular mechanisms of lipid-lowering activity of curcumin are based on gastrointestinal intake of cholesterol from dietary substances and reduction of cholesterol transfer to the circulatory system. For such suggestion, Niemen-Pick C1-like proteins, which are located on the gastrointestinal epithelial cells, were studied as molecular targets and it has been proven that curcumin can suppress its expression (Zhao *et al.*, 2012).

Wassmann *et al*. suggested that curcumin can induce cholesterol efflux through the system of transcription factors such as peroxime proliferators-activated receptors (PPARs). These transcription factors are a series of ligand-activated factors which occur in three different isoforms of PPARα, PPARδ, and PPARγ. When PPARγ is activated by a certain ligand, it induces ligand X receptors (LXR-α) and these processes lead to reverse cholesterol transport (Wassmann *et al.*, 2002).

Furthermore, it has been shown that curcumin regulates the activity of cavelion-1, a protein that is able to form cholesterol transport complex with different elements in the cell membrane. Such complex became attached to free cholesterol and regulates transport of additional cholesterol to the HDL particles (Yuan *et al.*, 2008).

Recent findings suggest that curcumin is involved in the modulation of different enzymes and proteins, not just single target gene, as previously suggested. Intake of curcumin regulates enzymes cholesterol 7α-hydroxylase or cytochrome P450 7A1 (CYP7A1), leading to a reaction with PPARɣ, LXR, and RXR and biodegradation of cholesterol. Many molecular targets have been described as the primary targets of curcumin activity, which leads to reduction in plasma cholesterol concentration and modulation of enzyme CYP7A1 has so far shown the most significant reduction in cholesterol concentrations (Kim and Kim, 2010).

Peschel *et al.* have shown that curcumin induces HMG-CoA reductase expression, an enzyme involved in cholesterol synthesis (Peschel *et al.*, 2007), while Shao *et al.* suggested that curcumin decreased the enzyme activity of HMG-CoA reductase (Shao *et al.*, 2012).

Many enzymes involved in lipid metabolism undergo modifications by curcumin. Such an enzyme is AMP-activated protein kinase (AMPK) stimulated by curcumin to interrupt fatty acid synthetic pathway (Kim and Kim, 2010). Shao *et al.* have described that curcumin reduces the level of malonyl-CoA by stimulating carnitine palmitoyl transferase-1 (CPT-1) and involves in β-oxidation. Malonyl-CoA is formed during fatty acids synthesis, and inhibits CPT-1 used to transfer fatty acyl CoA into mitochondria for β-oxidation. These processes lead to interruption of fatty acids pathway synthesis (Shao *et al.*, 2012).

CONCLUSION

The overall assessment demonstrates that curcumin is a potential candidate for the treatment of different cardiovascular diseases due to its diverse and complex multi molecular targets. The interest in pharmacological properties and the use of curcumin is rapidly growing.

The pharmaceutical industry seeks more efficient solutions and focuses on natural products such as curcumin itself. Phytotherapy is becoming more popular due to demonstrated evidence on efficiency and safety of natural products. Curcumin can play a significant role in the treatment of hyperlipidemia due to its ability to reduce total cholesterol and triglycerides. Furthermore, curcumin can improve lipid profiles by different molecular mechanisms and secure its role as one of the protective cardiovascular agents. Current clinical trials will provide a deeper understanding of the therapeutic potential of curcumin in the treatment and prevention of hyperlipidemia and will help to place this fascinating molecule at the fore front of novel therapeutics.

DISCLOSURE:

The authors have no disclosures or other conflicts of interest to this paper.

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Summary/Sažetak

Povećana vrijednost lipida (hiperlipidemija) predstavljaju jedan od osnovnih faktora rizika u nastanku različitih kardiovaskularnih oboljenja. Medikamentozna terapija hiperlipidemija obuhvata veliki izbor lijekova iz grupe hipolipemika, koji su dokazano farmakološki efikasni lijekovi. Međutim, svaka medikamentozna terapija sa sobom nosi rizik od nastanka neželjenih dejstava usljed primjene određene količine lijekova. Posljednih godina, a s ciljem da se uklone ili smanje neželjena dejstva sintetičkih lijekova, prednost se daje ispitivanju prirodnih supstance ili fitonutritienata koji čine osnov fitoterapije utemeljene na dokazima. Kurkumin, aktivna supstanca iz biljke *Curcuma longa* L. je od davnina poznat po svojim ljekovitim svojstvima, te do danas privlači pažnju istraživača. Dokazano je da kurkumin ispoljava različita farmakološka djelovanja, uključujući i antihiperlipidemijsko djelovanje. Cilj ovog rada je opisati osnovna fitohemijska svojstva kurkumina, prikazati njegove osnovne molekularne mehanizme hipolipidemijske aktivnosti, te naglasiti opravdanost upotrebe kurkumina kao zamjenske ili dopunske terapije hiperlipidemija.

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Experimental and theoretical study of Aspartic acid

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Abstract: The aim of this research is to detect zwittterionic structure of the aspartic acid and confirm the experimental spectra with quantum chemical calculations. The experimental IR and Raman spectra of aspartic acid powder show no vibrational bands of OH and NH stretching in expected spectral region. We assume that zwitterionic structure of aspartic acid is responsible for lowering the frequencies of these vibrations. An extensive experimental and computational research supports this assumption. Our DFT calculation strongly suggests the need for the dielectric environment in order to stabilize the zwitterionic structure of a single molecule. The network of intermolecular hydrogen bonding between aspartic acid molecules provides this dielectric environment. The DFT quantum mechanical calculations corroborate this assumption by optimizing a four-member group of molecules, which also gives an explanation of broad IR spectrum lines.

INTRODUCTION

Aspartic acid is one of the twenty amino acids which together form the basic building blocks of proteins, enzymes and other body tissues. Proteolytic enzymes known as aspartic proteases each possess two aspartic acid residues at the active site. Aspartic acid provides the amino group in the urea cycle and in the biosynthesis of purine and synthesis of pyramidine (Garett and Grisham, 2010). It is a precursor of the pyrimidine nucleotides and, in addition, is a key precursor for the synthesis of asparagine, methionine, lysine, threonine, and isoleucine (Garett and Grisham, 2010). It is known that these amino acids are participating in a variety of biochemical reactions, basic energy transfer and muscle activity and they are used for medical, cosmetic and industrial purposes (Zhu et al., 2011, Patil et al., 2018). It is also found that at higher concentrations aspartic acid affects the lifetime of the initial phase of $CaCO_3$ crystallization, the amorphous calcium carbonate, through the inhibition of crystal nucleation and growth (Tobler et al., 2014). The knowledge of the vibrational spectra of amino acids is very useful for lots of biochemical studies involving enzymes, proteins and their reactions (Navarrete, Hernández and Ramírez, 1994, Kumar, 2016, Numata et al., 2017). Several authors have demonstrated that the most stable structure for a free amino acid molecule is the nonzwitterionic form (NH2-CHR-COOH) (Alam and Ahmad, 2012), but it is possible to find a local minimum for the zwitterionic form (NH3+-CHR-CO2-) and the calculated frequencies were compared to IR and Raman spectra (Navarrete, Hernández and Ramírez, 1994, Freire et al., 2017, Silva et al., 2015). The molecule structure in solid state has been determinate by x-ray diffraction techniques and it occurs in the crystal as a zwitterion (Derissen, Endeman and Peerdeman, 1968). Single molecule has the absolute minimum of energy in the non zwitterionic structure but the zwitterionic structure is stabilized with other amino acid molecules in the solid state or with the solvent molecules in a solution (Navarrete, Hernández and Ramírez, 1994, Paxton and Harper, 2004, Nagy and Noszál, 2000). That property is also observed with smaller amino acids such as alanine and glycine (Ilijima, Tanaka and Onuma, 1991, Alper, Dothe and Coker, 1991, Ilijima and Beaglev, 1991, Gontrani, Mennucci and Tomasi, 2000).

Structure of the aspartic acid molecule in a solution also depends on the pH value of the solution (Paxton and Harper, 2004, Castro et al., 1995).

Our motivation to further contribute to this well explored subject is twofold. First, we have noticed there are no vibrational bands of OH and NH stretching in expected experimental spectral region. One possible explanation, as given in literature (Navarrete, Hernández and Ramírez,

1994), is in vast number of intermolecular hydrogen bonds. However, to apply this explanation on bands at 2510, 2661 and 2729 cm^{-1} the required frequency shift would be over 1000 cm^{-1}. The shift of such magnitude ascribed to hydrogen bonding is not commonly found. We argue that alongside hydrogen bonding there are quasi-free proton movements between two oxygen atoms and oxygen and nitrogen atoms. Second, our IR spectra of powder sample persistently showed broad bands, in spite of good spectrometer`s resolution of 1 cm^{-1}.

MATERIALS AND METHODS

The supplier of ≥ 98% L-aspartic acid was Sigma-Aldrich. To observe interactions experimentally, powder sample was characterized by attenuated total reflectance Fourier transform infrared spectroscopy (ATR FTIR), with Bruker Vertex 70 instrument. The absorbance data were collected between 400 and 4000 cm^{-1} with spectral resolution of 1 cm^{-1} and average of 32 scans. Raman spectra were recorded at room temperature with microtriple grating spectrometer Horiba Jobin Yvon model T64000. The spectra were excited by 514.5 nm line of the Coherent INNOVA-400 argon ion laser. Laser power at the sample was 7 mW.

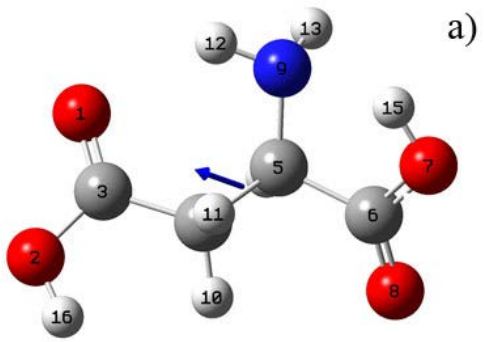
Calculations

The quantum chemical calculations were performed with the Gaussian 09 package program at DFT–B3LYP level of theory (Frisch et al., 2009). The standard 6-311++G(d,p) basis set was used to carry out the calculation of molecular geometries, force fields, vibrational frequencies, as well as IR intensities and Raman activities.

RESULTS AND DISCUSSION

The molecule of aspartic acid is composed of 16 atoms and it does not have any molecule symmetry.

It is well known from experimental research (Navarrete, Hernández and Ramírez, 1994) that aspartic acid (ASP) takes zwitterionic form. But DFT calculations of single free molecule fail to give zwitterionic form (Tobler et al., 2014).



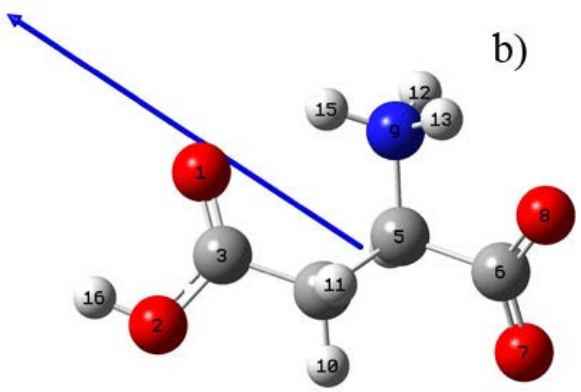


Figure 1. a) Single free molecule of aspartic acid. b) Zwitterionic structure of aspartic acid. The blue arrow line represents dipole moments

For a single free molecule (ε = 1), the only way to obtain its zwitterionic structure is to place it in dielectric environment. Our first attempt was to calculate it in aqueous environment, by setting the relative dielectric constant to 82. Detailed inspection of relative dielectric constant set the low limit around ε = 3 for stability of zwitterionic structure.

The dipole moments of these two forms significantly differ in magnitude but not in direction. Just for comparison, the dipole moment of single free molecule is 1.6 D and for zwitterionic conformation is around 7 D for ε = 3 (Fig. 1).

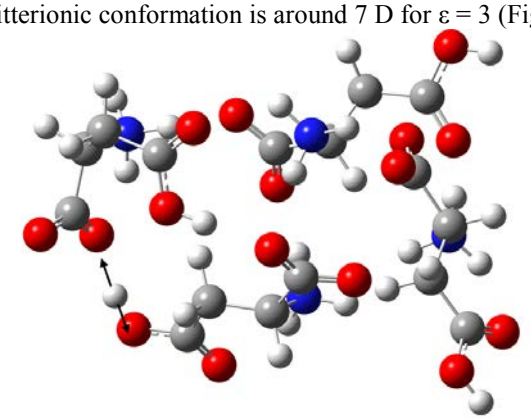


Figure 2. Optimized structure of four aspartic acid molecules in zwitterionic conformation. The arrows show proton movement in intermolecular hydrogen bonding corresponding to bands in the 2500 – 2700 cm^{-1} range

Further calculations show that even a small group of molecules creates a necessary dielectric environment which makes all molecules stable in zwitterionic form. In other words, the dielectric environment is self-induced with sufficient dielectric constant. In Figure 2 an optimized geometry for a group of four molecules is shown in zwitterionic form without any specified environment.

Stretching of OH and NH groups in our calculations of quadrimer structure have lowered significantly from the values calculated for one zwitterionic ASP molecule. For hydroxy groups surrounded with other molecules, the shifts are in the 600 – 1000 cm^{-1} frequency range. The most IR intensive amino groups stretching have lowered from approximately 3400 cm^{-1} to the 3000 and even to the 2700cm^{-1}. One part of the lowered hydrogen bonding vibrational modes falls in the region of CH and CH_2 stretching. The other part of these modes is lowered even

more, up to the 2500 cm^{-1}. If the hydroxy or amino group is on the edge of the cluster, there is no shift, which can be explained by the lack of the influence of surrounding molecules.

Our biggest calculated cluster consists of four ASP molecules because of numerical limitations. In our powdered sample, we presume that clusters consist of larger number of ASP molecules. Because of that, number of "marginal" hydroxy and amino groups is small in comparison to the hydroxy and amino groups that are surrounded with other molecules. That is consistent with the experimental spectra of powdered samples, in which there are no OH and NH stretching bands at expected frequencies, around 3600 cm^{-1} and 3400 cm^{-1} respectively (Figure 3). But there exists a broad line around 3000 cm^{-1} consisting of CH stretching overlapping with lowered OH and NH stretching. Bands at 2510, 2661 and 2729 cm^{-1} (Figure 3) can be explained as OH stretching in intermolecular hydrogen bonding within the cluster (Stuart, 2004). Our calculations show these bands correspond to proton movement between O-O and O-N atoms (Figure 2).

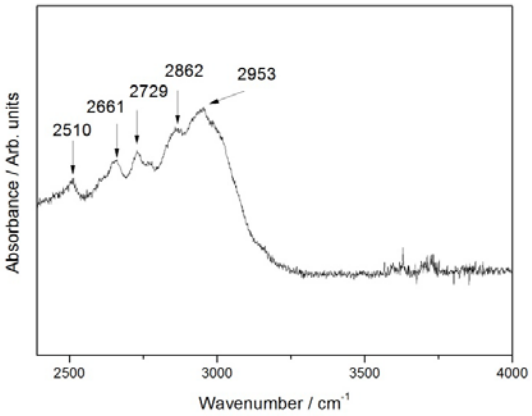


Figure 3. Infrared spectrum of aspartic acid in the 2400 – 4000 cm^{-1} region

Bands at 2510, 2661 and 2729 cm^{-1} are interpreted as belonging to proton movements between two oxygen atoms or between oxygen and nitrogen atoms. Higher bands belong to CH and lowered OH stretching.

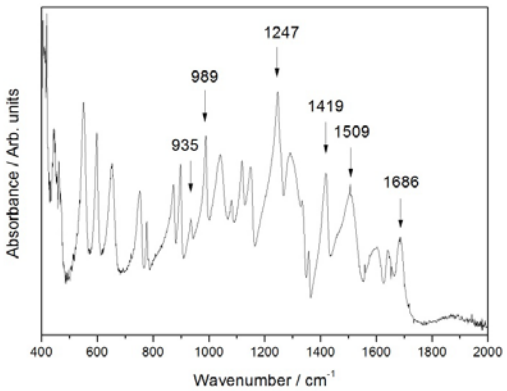


Figure 4. Infrared spectrum of aspartic acid in the 400 – 2000 cm^{-1} region

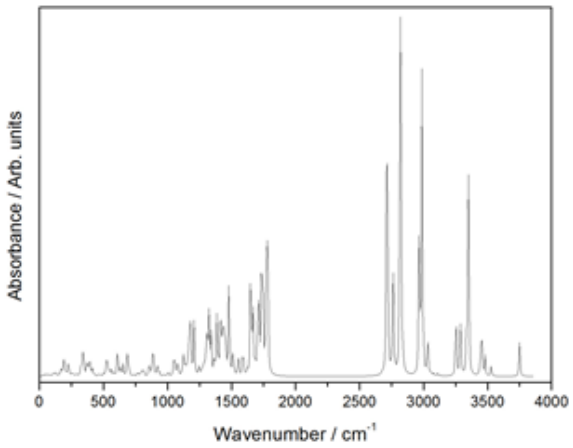


Figure 5. Calculated infrared spectrum of four members cluster presented in Fig. 2

The main characteristic of our observed infrared spectrum is a composition of broad vibrational bands (Figure 3 and 4). Calculated IR spectrum of aspartic acid cluster also shows grouping of bands (Figure 5). Same vibrations in different molecules of the sample have slightly different frequencies. That is consistent with broader bands observed in experimental FTIR spectra.

Infrared and Raman spectra presented at Figures 4, 6 and 7 show vibrational bands assigned to NH3+ group vibrations. Calculated and observed vibrational modes for zwitterionic form of aspartic acid molecule are presented in Table 1. Broad IR band at 1509 cm^{-1} belongs to NH3+ asymmetrical bending. In the frequency range from 989 to 1247 cm^{-1}, we observe, both in IR and Raman spectra, NH3+ rocking combined with other modes. This is generally consistent with the results of past research although they have used different computational method (Navarrete, Hernández and Ramírez, 1994.)

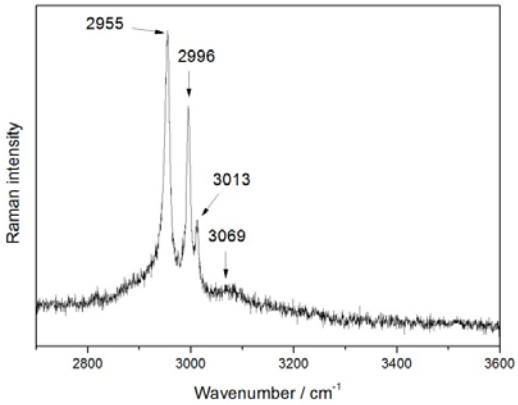


Figure 6. Raman spectrum of aspartic acid in 2700 – 3600 cm^{-1} region

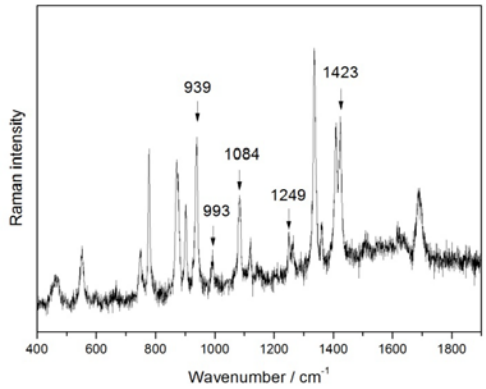


Figure 7. Raman spectrum of aspartic acid in 400 – 1900 cm^{-1} region

Table 1. Calculated and observed frequencies (cm^{-1}) for zwitterionic form of aspartic acid molecule

	Observed[a]			
	IR	Raman	Calculated[b]	Vibrational mode
1			3722	OH str
2			3507	NH str
3			3353	NH_3 asym str
4		3069 w	3279	NH_3 sym str
5	3018 w, sh	3013 m	3136	CH_2 asym str
6	2985 w, sh	2996 vs	3127	CH str
7	2953, s	2955 vs	3037	CH_2 sym str
8	1686 s	1687 s	1743	C=O str, NH_3 asym bend
9	1641 m, broad	1640 w	1674	NH_3 asym bend, COO^- asym str
10		1618 w	1661	COO^- asym str, NH_3 asym bend
11	1507 s, broad	1508 w	1626	NH_3^+ asym bend
12	1459 w, sh	1462 w	1460	CH_2 sciss
13	1419 s	1423 s	1434	NH_3^+ sym bend
14	1408 sh	1409 s	1406	CO str, OH bend, CH_2 wag, CC str, CH bend
15	1358 m	1362 m	1396	CH bend
16	1334 m	1335 s	1350	CC str, COO^- sym str, NH_3 sym bend, CH bend
17	1291 broad		1330	CH_2 wagg, OH bend, CH bend
18	1258 sh	1263 w	1281	CH_2 twist, OH bend, CH band
19	1247 s	1249 m	1250	CH_2 twist, CH bend, NH_3 rock, COH bend
20	1149 m	1143 w	1183	OH bend, CH bend, NH_3 rock, CO str, CH_2 twist
21	1118 m	1121 m	1142	CH bend, NH_3 rock,CH_2 twist, OH bend
22	1081 w	1084 m	1103	NH_3 rock, CH bend, CH_2 twist
23	1042 m broad		1049	CN str, CC str
24	989 s	995 m	964	CC str, NH_3 rock
25	935 w	939 s	928	CC str, CCC bend
26	897 m	903 m	870	CC str, COH bend
27	872 m	872 s	843	CN str, CC str
28	777 m	778 s	765	OCO^- out of plane bending
29	752 m	752 m	725	OCOH out of plane bending,COO^- in plane bend.
30	653 m	658 vw	664	OCOH out of plane bending
31	598 s	600 vw	622	OCOH out of plane bending
32	550 s	552 m	551	OCOH out of plane bending

a Observed in IR and Raman spectra of aspartic acid powdered sample. Abbreviations used: s, strong; m, moderate; w, weak; v, very; sh, shoulder

b The computed nonscaled values are calculated using B3LYP/6-311G++(d,p) method.

Table 2. The most relevant vibrational modes and frequencies (cm^{-1}) of group of four aspartic acid molecules

Calculated		Observed		
ASP quadrimer	ASP zwitterionic	IR	Raman	Vibrational mode
3751, 3749, 3351, 2821	3722			OH stretching
3527, 3481, 3456, 3447, 3336, 3290, 3254, 3031, 2988, 2966, 2762, 2714	3507, 3353, 3279			NH stretching
1650, 1623, 1590, 1553	1626	1509 s	1508 w	NH_3^+ asymmetric bending
1512, 1484, 1478, 1443	1434	1419 s	1423 s	NH_3^+ symmetric bending
1185, 1176, 1051, 893	1183	935 w	939 s	OH in-plane bending OH out-of-plane bending

The vibrational modes shown in Table 2 can explain broadening of observed infrared bands. As can be seen, the calculated frequencies of a four-member group can have a bandwidth of around 100 cm^{-1}. The broadening is mostly emphasized for NH3+ asymmetric bending.

A strong Raman band at 939 cm^{-1} is empirically assigned to OH out-of-plane bending (Zhu et al., 2011, Navarrete, Hernández and Ramírez, 1994, Castro et al., 1995). The calculation performed on single zwitterionic molecule shows very weak presence of this mode which is significantly entangled with skeletal vibrations, but shows strong presence of OH in-plane mode at 1183 cm^{-1}. However, the calculation performed on aspartic acid quadrimer shows both OH in-plane and OH out-of-plane bending as strong modes. The OH groups on cluster's border show in-plane bending at higher frequencies (1185 and 1176 cm^{-1} are very close to 1183 cm^{-1} belonging to single zwitterionic molecule) while the OH group in the cluster's interior clearly show out-of-plane bending at significantly lower frequencies which are in agreement with observed frequencies (see Table 2).

CONCLUSION

The main points of this work can be summarized as:

- The OH and NH stretching modes frequencies are significantly shifted to lower values within the powder of aspartic acid. Both experimental and calculated spectra prefer zwitterionic form of aspartic acid molecules.
- The DFT optimization of a single ASP zwitterionic molecule can be achieved only in dielectric environment with $\varepsilon r \geq 3$. The optimization of a group of aspartic acid molecules in zwitterionic form is possible due to the self-induced dielectric environment.
- The grouping of molecules is responsible for broadening of vibrational bands in infrared spectrum. This is confirmed by DFT calculations.
- The complexity of intermolecular hydrogen bonding is the main cause for the broadening of spectral lines and their significant shifting to lower values.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally.

‡Andrej Vidak, ‡Iva Movre Šapić, ‡Vladimir Dananić.

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Summary/Sažetak

Cilj našeg istraživanja je detekcija zwitterionske strukture asparaginske kiseline i potvrđivanje eksperimentalnih spektara s kvantno kemijskim proračunima. Eksperimentalni IR i Raman spektri asparaginske kiseline u prahu ne pokazuju OH i NH vibracijske vrpce u očekivanom spektralnom području. Pretpostavljamo da je zwitterionska struktura asparaginske kiseline odgovorna za snižavanje frekvencija tih vibracija. Opsežna eksperimentalna i računalna istraživanja podupiru tu pretpostavku. Izračun DFT-a snažno upućuje na potrebu za dielektričnom okolinom kako bi se stabilizirala zwitterionska struktura jedne molekule. Mreža intermolekularnih vodikovih veza između molekula asparaginske kiseline osigurava ovo dielektrično okruženje. DFT kvantno-mehanički izračuni potkrjepljuju ovu pretpostavku optimiranjem četveročlane skupine molekula, što također daje objašnjenje širokih linija IR spektra.

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Investigation of Inhibitory Effect of the *Aloe Vera* Extract on Corrosion of Aluminium Alloys

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Abstract: This paper considers the inhibition effect of Aloe Vera on the selected aluminium alloys in 10 % sulfuric acid and 3 % sodium chloride solutions at room temperature, using methods of potentiodynamic polarisation and cyclic voltammetry. The study involved as-cast and heat-treated 2xxx alloys, with the scanning speed of 1mV/s for linear polarisation and 50 mV/s for cyclic voltammetry. The various constant potential was applied for each tested alloy. Polarisation results indicate that the transpassivation occurs in an acid medium in case of each alloy. The obtained results indicate that Aloe vera extract acts as a cathodic inhibitor.

INTRODUCTION

Aluminium alloys, in the 2xxx series, based on copper and magnesium addition find application in the production of trucks, aircraft wheels, fuselage and wing skins, as well as various structural parts (Davis, 2001). Copper is added for increasing the strength, hardness, fatigue and creep resistance as well as for castability improvement of aluminium alloys (Al-Rawajfeh *et al.*, 2009). The optimal mechanical properties of 2xxx alloys similar or even better compared to low carbon steel could be achieved by heat treatment (Davis, 2001). Further improvement of strength during solution heat treatment and quenching may be caused by the addition of magnesium (Hatch, 1984). On the other hand, microstructural changes leading to better mechanical properties may result in a decrease in corrosion resistance of 2xxx alloys (Ghosh *et al.*, 2013). The oxide film formed while exposing the aluminium surfaces to different environmental conditions protects it from further oxidation (Davis, 1999). However, in highly acidic, or alkaline solutions, especially ones containing chloride ions, the oxide layer is unstable and it is destroyed (Xhanary *et al.*, 2017). The corrosion resistance of 2xxx alloys is often good but lower than most aluminium alloys (Hikmat *et al.*, 2014). Strong electrochemical effects on corrosion of 2xxx alloys may be caused by a more significant change in electrode potential with copper content in solid solution as well as non-uniformities in solid-solution concentration (Davis, 1999). In order to reduce corrosion progress of aluminium alloys in various environments inhibitors are commonly used (Ouchenane *et al.*, 2014, Hamdou *et al.*, 2017, Umoren *et al.*, 2009, Oguzie, 2007, Avwiri *et al.*, 2003, Lamaka *et al.*, 2007, Zheludkevich *et al.*, 2005, Al-Turkustani *et al.*, 2010).
The inhibitors retard or prevent the corrosion process by reducing the anodic or cathodic polarisation behaviour (decreasing the value of Tafel coefficients). Hence, the movement or diffusion of ions to the metallic surface is decreased and the electrical resistance of the metallic surface is increased. The inhibitors decrease the corrosion rate by adsorption of ions or molecules on the metal surface (Gerengi *et al.*, 2014). Various organic and inorganic compounds usually dissolved in aqueous environments may be used as inhibitors (Fayomi *et al.*,

2018). Although phosphates, chromates, dichromates, silicates, bromates and arsenates are popular inorganic inhibitors, their toxic effects on the environment are recognised (Khadraoui *et al.*, 2013). Therefore, the application of non-toxic organic inhibitors is encouraged (Hamdou *et al.*, 2017). The investigations focused on synthesising the environmental friendly chemical compound with low cost which could be used as inhibitors have shown that plant extracts from leaves, seeds, heartwood, bark, roots or fruits inhibit the corrosion of metals in acidic solutions (Khadraoui *et al.*, 2013). *Aloe Vera* leaves containing various active compounds may be used for the production of green inhibitor for corrosion of aluminium alloys (Xhanary *et al.*, 2017, Al-Turkustani *et al.*, 2010, Fayomi *et al.*, 2018).

In this work, the inhibition effect of *Aloe Vera* extract at the different concentration on corrosion behaviour of two 2xxx aluminium alloys in 10 % sulfuric acid and 3 % sodium chloride solutions has been studied using potentiodynamic polarisation and cyclic voltammetry technique.

EXPERIMENTAL

Two 2xxx alloys with the composition shown in Table 1 were prepared by melting commercially pure (99.4 %) aluminium, technically pure copper, magnesium, zinc and nickel as well as pre-alloy AlMn60 (Al-60 % Mn). The melting was carried out in a 5.5-kW electric resistance furnace using a graphite crucible. For the fluxing of the melts, a TAL – 2 was added in the amount of about 2 % of their quantities. Hexachloroethane tablets were used for the degassing the melts in the amount approximately equal to 0.25 % of each melt quantity. The pouring of the melts into the metal moulds was carried out at 740 °C. As-cast specimens of alloys were solution treated at 505 °C ± 5 °C for 6 hours followed by quenching in water (at 80 °C). The subsequent ageing treatment was performed at 200 °C ± 5 °C for 7 hours while specimens were finally cooled in ambient air.

Table 1. Chemical composition of 2xxx alloys

Alloy	Fe (%)	Si (%)	Cu (%)	Zn (%)	Mn (%)	Mg (%)
A	0.37	0.22	4.78	0.65	0.048	0.71
B	0.41	0.22	5.36	0.64	0.38	1.45

The samples for corrosion tests were cut from the as-cast and heat-treated specimens and then ground with silicon carbide abrasive papers and cleaning in acetone. The electrochemical tests were conducted at room temperature in 10 % sulfuric acid and 3 % sodium chloride solutions by performing a potentiodynamic polarisation test and cyclic voltammetry. In that sense, the potentiostat/galvanostat 263 A and 5210 Lock-in Amplifier supplied with Power CV software was used. The electrochemical measurements were performed in a cell containing a saturated Ag/AgCl electrode as a reference electrode and the platinum electrode as the counter electrode, while the specimens of 2xxx alloys were used as the working electrode. *Aloe vera* plant leaves from Kiseljak area in the amount of 0.5 kg were used for the preparation of inhibitor. The extract was obtained by the Soxhlet extraction method in the aqueous solution, with the initial concentration of 20 mg/ml. *Aloe Vera* inhibitor was added to 10 % sulfuric acid as well as 3 % sodium chloride solutions at concentrations of 0.0266 mg/ml, 0.0533 mg/ml and 0.08 mg/ml. Tafel extrapolation method was used for obtaining the potentiodynamic polarisation curves of the examined alloys over the range from -1.5 V to + 1 V related to open circuit potential (OCP) at a scan rate 1 mV/s. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (j_{corr}), anodic Tafel slopes (β_a) as well as cathodic Tafel slopes (β_c) are determined using the software installed in the instrument.

The corrosion inhibition efficiency (in percentage) was calculated using the following equation:

$$\eta = \frac{j_{corr} - (j_{corr})_{inh}}{j_{corr}} \cdot 100 \qquad (1)$$

where j_{corr} and $(j_{corr})_{inh}$ represent corrosion current density values without and with inhibitor, respectively.

The cyclic voltammetry was used to examine the diffusion processes between the electrolytes and the layer on the surface of the electrode. All cyclic voltammetry tests were performed in 10% sulfuric acid solution over the potential range -0.5 V to 0.7 V, at a scan rate of 50 mV/s.

RESULTS AND DISCUSSION

The polarisation behaviour of as-cast and heat-treated specimens of 2xxx alloys in 10 % sulfuric acid and 3 % sodium chloride solutions in the absence and presence of *Aloe vera* extract is given in Figures 1 to 4. The Tafel extrapolations of the corrosion current density (j_{corr}), the corrosion potential (E_{corr}) as well as values of anodic Tafel slopes (β_a) and cathodic Tafel slopes (β_c) are shown in Tables 2 to 5. The inhibition efficiencies of various concentrations of *Aloe vera* extract for corrosion of 2xxx alloys in 10 % sulfuric acid solutions and 3 % sodiumchloride solutions are presented in Tables 6 and 7, respectively.

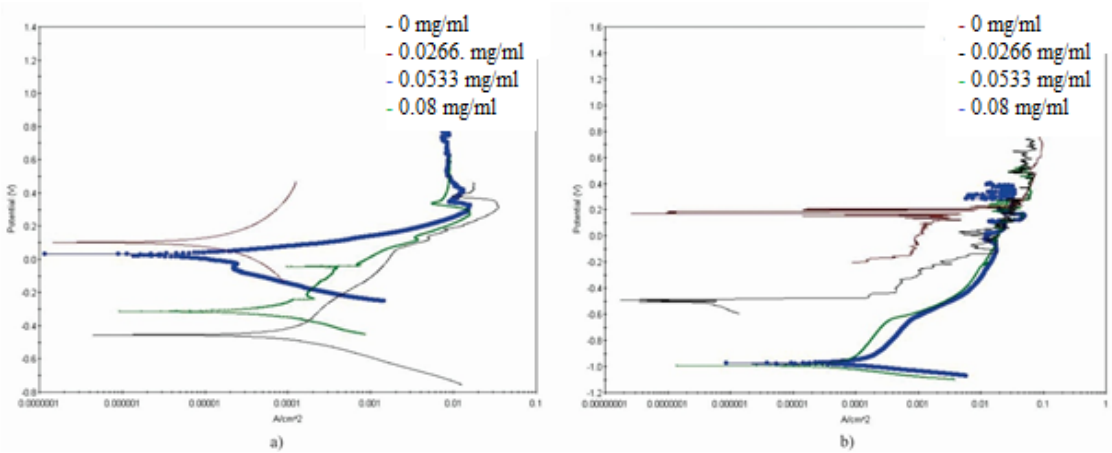

Figure 1. Potentiodynamic polarisation curves for as-cast alloy A in 10 % sulfuric acid solutions (a) and 3 % sodium chloride solutions (b) without and with various concentration of *Aloe vera* extract

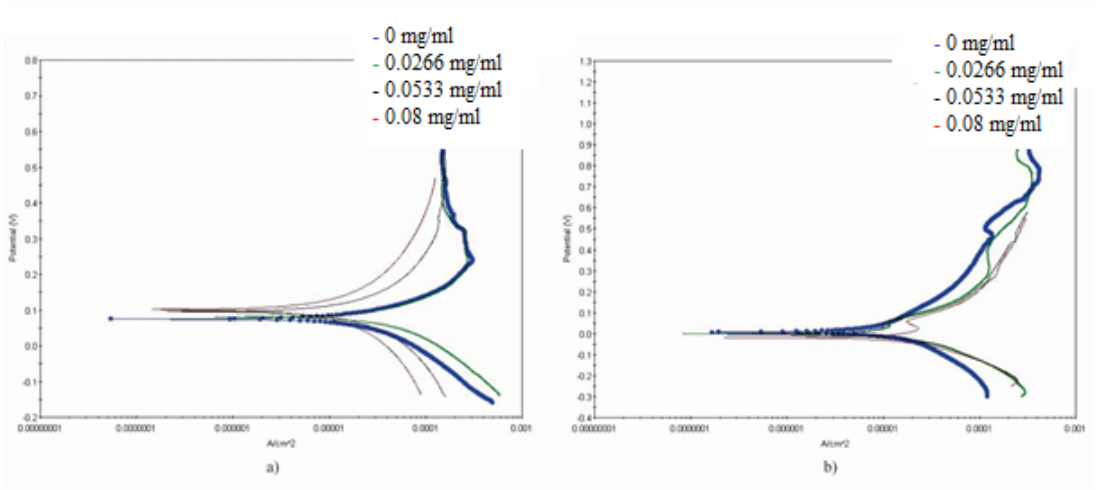

Figure 2. Potentiodynamic polarisation curves for heat-treated alloy A in 10 % sulfuric acid solutions (a) and 3 % sodium chloride solutions (b) without and with various concentration of *Aloe Vera* extract

Table 2. Potentiodynamic polarisation parameters for the corrosion of the as-cast and heat-treated specimens of alloy A in 10 % sulfuric acid solutions containing different concentrations of the *Aloe Vera* inhibitor

Alloy A	***Aloe Vera* extract (mg/ml)**	**E (mV)**	**I_{corr} (μAcm^{-2})**	**β_c ($mVdec^{-1}$)**	**β_a ($mVdec^{-1}$)**
As-cast samples	Without inhibitor	12.851	7.348	142.481	54.283
	0.0266	- 327.336	9.609	117.880	358.659
	0.0533	- 460.290	6.951	134.933	387.645
	0.0800	- 482.789	1.591	142.929	383.931
Heat-treated samples	Without inhibitor	44.114	56.71	230.110	264.931
	0.0266	94.521	57.16	239.047	150.408
	0.0533	96.249	24.12	234.713	254.806
	0.0800	102.824	12.31	200.881	217.258

Table 3. Potentiodynamic polarisation parameters for the corrosion of the as-cast and heat-treated specimens of alloy A in 3 % sodium chloride solutions containing different concentrations of the *Aloe Vera* inhibitor

Alloy A	***Aloe Vera* extract (mg/ml)**	**E (mV)**	**I_{corr} (μAcm^{-2})**	**β_c ($mVdec^{-1}$)**	**β_a ($mVdec^{-1}$)**
As-cast samples	Without inhibitor	137.113	19.60	210.721	365.493
	0.0266	- 576.873	12.22	132.922	443.708
	0.0533	- 920.252	2.443	235.212	256.828
	0.0800	- 987.835	1.322	58.731	434.836
Heat-treated samples	Without inhibitor	14.690	18.11	237.467	551.970
	0.0266	13.177	9.484	116.624	234.630
	0.0533	11.309	8.640	104.450	181.084
	0.0800	9.364	1.277	123.885	229.973

The decrease in the corrosion current density with inhibitor addition to 10 % sulfuric acid solutions and 3 % sodium chloride solutions was detected for almost all as-cast and heat-treated specimens of alloy A with 4.78 % of copper and 0.71 % of magnesium (Figures 1 and 2, Tables 2 and 3). However, compared to corrosion examinations without inhibitor, the slight increase in the corrosion current density was detected for as-cast and heat-treated samples of alloy A studied in 10 % of sulfuric acid solution with an inhibitor concentration of 0.0266 mg/ml (Table 2). The values of corrosion potential of as-cast specimens of alloy A exposed to 10 % sulfuric acid and 3 % sodium chloride solutions were shifted to the more negative side with the addition of *Aloe vera* extract (Table 3). In the work of Al-Turkustani *et al.*, 2010 who examined the effect of *Aloe vera* extract on aluminium corrosion in hydrochloric acid solutions, the instantaneous and rapid attack of the oxide film by chloride ions was pointed out. The corrosion reaction was accelerated by chloride ions due to obstruction of the reparation of oxide protective film and forming the intermediate soluble complex (Al-Turkustani *et al.*, 2010). The dissolution of aluminium ions (atoms) from lattice to the solution was facilitated by formed complexes leading to the passive layer on the metal surface and pitting corrosion (Al-Turkustani *et al.*, 2010). The difference in the effect of the *Aloe Vera* extract on corrosion behaviour of carbon steel compared to aluminium alloys has been demonstrated in the work of Sribharathy et al., who indicated that the *Aloe Vera* controlled the anodic reaction predominantly by forming Fe^{2+} complex on the anodic sites of the metal surface in acid solution (Sribharathy *et al.*, 2013). In our work, we have a controlled formation of an aluminium complex on a metal surface.

Regarding heat-treated samples of alloy A, it could be seen that with the increasing concentration of *Aloe vera* extract, the corrosion potential was shifted toward positive values for samples examined in 10 % sulfuric acid solutions, while its shift towards negative direction was recorded for those studied in 3 % sodium chloride solutions. It may be seen that alloy A is more stable in its heat-treated condition and exhibits transpassivation, meaning the measurements are made in the region of the anode polarisation. Also, it can be observed that there is no significant inhibition of the anode process, due to the occurrence of the anodic passivity of the metal. Moreover, better inhibition effects of *Aloe vera* extract on corrosion of heat-treated specimens have been recorded compared to as-cast samples of alloy A. The anodic polarisation should be noted, while cathodic polarisation is observed only at a concentration of 0.08

mg/ml. What also can be pointed out with a view to the inhibitory effects on this type of alloy is that in case of any concentration, both passivation and transpassivation of metal occur.

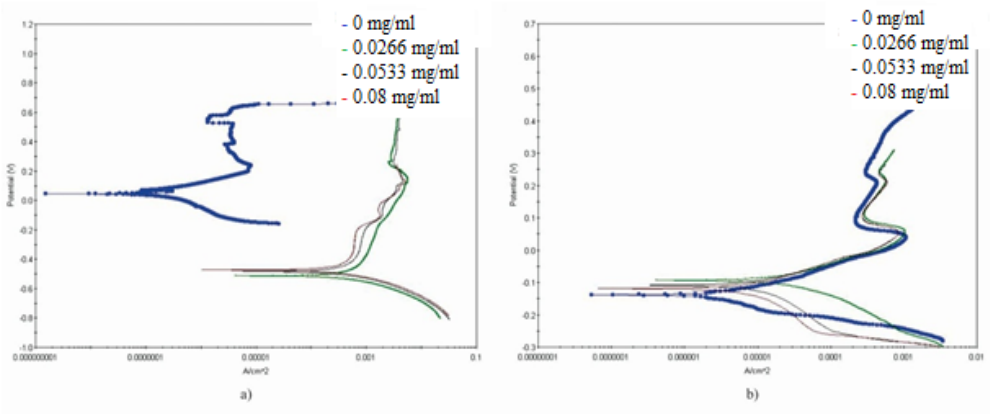

Figure 3. Potentiodynamic polarisation curves for as-cast alloy B in 10 % sulfuric acid solutions (a) and 3 % sodium chloride solutions (b) without and with various concentration of *Aloe vera* extract

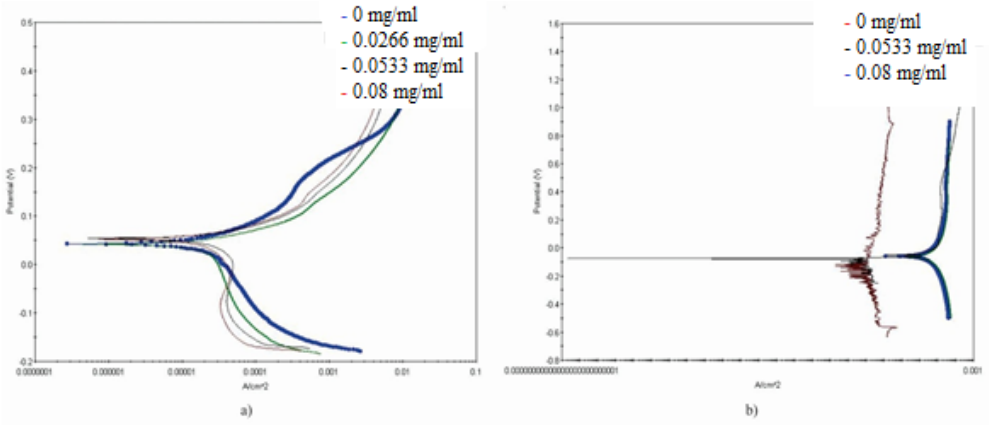

Figure 4. Potentiodynamic polarisation curves for heat-treated alloy B in 10 % sulfuric acid solutions (a) and 3 % sodium chloride solutions (b) without and with various concentration of *Aloe vera* extract

Table 4. Potentiodynamic polarisation parameters for the corrosion of the as-cast and heat-treated specimens of alloy B in 10 % sulfuric acid solutions containing different concentrations of the *Aloe Vera* inhibitor

Alloy B	***Aloe vera* extract (mg/ml)**	**E (mV)**	**I_{corr} (μAcm^{-2})**	**β_c ($mVdec^{-1}$)**	**β_a ($mVdec^{-1}$)**
As-cast samples	Without inhibitor	54.019	18.34	138.590	95.431
	0.0266	- 509.571	46.87	126.506	553.129
	0.0533	- 484.440	44.27	112.901	663.232
	0.08	-494.562	28.93	58.769	489.303
Heat-treated samples	Without inhibitor	4.748	29.52	170.337	135.670
	0.0266	21.846	26.03	300.848	67.512
	0.0533	50.008	33.80	317.795	60.550
	0.08	38.135	24.71	173.695	68.278

Table 5. Potentiodynamic polarisation parameters for the corrosion of the as-cast and heat-treated specimens of alloy B in 3 % sodium chloride solutions containing different concentrations of the *Aloe Vera* inhibitor

Alloy B	[Inhibitor] mg/ml	E (mV)	I_{corr} (μAcm^{-2})	β_c ($mVdec^{-1}$)	β_a ($mVdec^{-1}$)
As-cast samples	Without inhibitor	- 145.052	2.560	51.471	60.685
	0.0266	- 94.290	2.849	85.117	88.749
	0.0533	- 113.321	1.414	169.156	89.263
	0.08	- 118.871	0.9181	159.267	87.531
Heat-treated samples	Without inhibitor	- 132.597	13.7	720.816	608.799
	0.0533	- 60.643	4.670	223.668	220.135
	0.08	- 57.875	6.293	428.513	441.673

Compared to the corrosion testing of as-cast alloy B containing 5.36 % copper and 1.45 % of magnesium in 10 % sulfuric solution without inhibitor, higher values of current density was observed when the examination had included the addition of *Aloe vera* extract (Figure 3a, Table 4). The decrease in current density of as-cast samples of alloy B was recorded with the addition of inhibitor to 3 % sodium chloride solutions except for inhibitor concentration of 0.0266 mg/ml (Figure 3b, Table 5). The study of heat-treated samples of B alloy has shown that the addition of *Aloe vera* extract of 0.0266 mg/ml and 0.08 mg/ml to 10 % sulfuric acid solutions has caused the decrease in the current density (Figure 4a, Table 4). Regarding examination without using inhibitor, lower values of current density were obtained for heat-treated specimens of alloy B tested in 10 % sodium chloride solutions with 0.0533 mg/ml and 0.08 mg/ml of *Aloe vera* extract (Figure 4b, Table 5). The corrosion potential of as-cast specimens of alloy B studied in 10 % sulfuric acid solution was shifted significantly to a more negative value with the addition of 0.0266 mg/ml of inhibitor. Further increase in the amount of inhibitor in 10 % sulfuric acid solutions has caused the negative value of corrosion potential of as-cast samples of alloy B too. However, the values of corrosion potential of heat-treated specimens of alloy B exposed to 10 % sulfuric acid solutions containing a different concentration of inhibitor are shifted toward positive direction compared to the corrosion examinations without inhibitor usage. Moreover, for as-cast and heat-treated specimens of alloy B, the values of corrosion potential were shifted to a more positive side in the presence of *Aloe vera* extract in 3 % sodium chloride solutions.

The study of corrosion behaviour of the alloy B in an acid medium in the absence of the inhibitor indicates cathodic reaction of the metal, i.e. the abrupt slow-down of the cathode process in achieving the certain potential of passivation, because of formation of the phase passive films on the cathodic surface (Figure 3a). When comparing linear polarisation shown in Figure 1b and Figure 3b, it is evident that in case of as-cast specimens of both 2xxx alloys in 3 % sodium chloride solutions, the specimens of alloy B exhibited more distinguished passivation and transpassivation. Also, any inhibitor concentration causes cathodic polarisation, while the adsorption of inhibitors achieved the passivation potential onto the surface of the alloy. In the case of alloy B, the maximal inhibitory effect (65.91 %) was achieved for heat-treated specimens exposed to 3 % sodium chloride solutions. The potential value for the inhibitor concentration of 0.0266 mg/ml can be attributed to the dissolving of phase particles (Lopez-Garrity *et al.*, 2014).

By comparison of Figure 2a and Figure 4a, it is evident that despite the different composition of 2xxx alloys, the thermal treatment did not affect the passivation in acid medium. The distinguished occurrence of transpassivation

process was not observed in examined alloys. Further on, the cathodic polarisation is recognised in both heat-treated alloys, while in the case of as-cast specimens of the alloy B, the adding of inhibitor resulted in anodic polarisation, meaning that the inhibitor reduced the corrosion rate of the tested alloy in the medium concerned, as shown in Figure 3a. The minor adsorption of the inhibitor on the surface of the anode and minor anodic passivation of heat-treated samples of alloy B in 3 % sodium chloride solutions were achieved (Figure 4b).

The obtained different values of the current density and corrosion potential with the variation of inhibitor concentration depend on molecules and substituents that form the structure of *Aloe vera*. The maximum value of inhibition efficiency of about 93.25 % was identified for alloy A exposed to 3 % sodium chloride solutions.

In the investigated system, the cathodic reaction is the evolution of hydrogen. Hence, if that reaction proceeds Tafel-Volmer mechanism, the value of the Tafel slope will be 118 mV/dec (Bockris *et al.*, 1974). The higher values of β_c obtained for the most examined specimens in 10 % sulfuric acid and 3 % sodium chloride solutions are consistent with the evolution of hydrogen at the electrode surface, which was covered by oxide film (Evans *et al.*, 1962) as well as the complex oxide-inhibitor. The Values of β_a are much higher than expected for uniform dissolution of aluminium giving the hydrated Al^{3+} ions (40 mV/dec). However, these values are comparable with the values of Tafel slope obtained for Al - electrode covered with oxide film (Hurlen *et al.*, 1984).

Table 6. Inhibition efficiency of various concentrations of *Aloe vera* extract for corrosion of 2xxx alloys in 10 % sulfuric acid solutions

Specimen	0.0266 *Aloe vera*	0.0533 *Aloe vera*	0.08 *Aloe vera*
As-cast samples of alloy A	-30.77%	5.40%	78.35%
Heat-treated samples of Alloy A	-0.79%	57.47%	78.29%
As-cast samples of alloy B	-60.87%	-54.52%	-36.60%
Heat-treated samples of Alloy B	11.82%	-14.50%	16.29%

Table 7. Inhibition efficiency of various concentrations of *Aloe vera* extract for corrosion of 2xxx alloys in 3 % sodium chloride solutions

Specimen	0.0266 *Aloe vera*	0.0533 *Aloe vera*	0.08 *Aloe vera*
As-cast samples of alloy A	37.65%	87.53%	93.25%
Heat-treated samples of Alloy A	47.63%	52.29%	92.95%
As-cast samples of alloy B	-11.30%	44.76%	64.13%
Heat-treated samples of Alloy B	/	65.91%	54.06%

As it can be seen from Tables 6 and 7, for some concentrations of *Aloe Vera* extract the inhibition effect was not recognised in 10 % sulfuric acid solutions. It could be the consequence of the occurrence of the reduction reactions and formation of the film on the electrode surface with molecules H_2O and SO_4^{2-} ions. The increase in corrosion current and dissolving of a passive film especially for as-cast specimens of alloy B are observed. Consequently, a uniform pitting corrosion occurs in the measured potential on the alloy surface.

On the contrary, *Aloe Vera* extract exhibited a strong inhibition effect in 3 % sodium chloride solutions meaning that it blocks corrosion spot on the alloy surface, which reduces the uniform corrosion and prevents forming of the pits. The significant inhibition influence is obvious for the alloys A and B in 10 % sulfuric acid and 3 % sodium chloride solutions containing *Aloe Vera* extract in a concentration of 0.0533 mg/ml and 0.0800 mg/ml. The reduced permeation currents in the presence of the inhibitors can be attributed to the slow discharge step followed by fast electrolytic desorption step:

$$M_{(e)} + H_3O^+ \text{ slow} \rightarrow MH_{ads} + H_2O \quad (2)$$

$$MH + H_3O^+ + M_{(e)} \text{ fast} \rightarrow 2M + H_2O + H_2 \quad (3)$$

The reduction of hydrogen uptake could be associated with the adsorption of the phytochemical constituents present in the plant extracts on the surface alloy, which prevented permeation of hydrogen into metal (Shyamala *et al.*, 2011).

The different values of the corrosion inhibition efficiency of *Aloe vera* extract in 10 % sulfuric acid solutions and 3 % sodium chloride solutions were evaluated depending on the chemical composition and condition of examined alloys (Tables 6 and 7). The higher inhibition efficiency of *Aloe Vera* extract was ensured in 3 % sodium chloride solutions compared to 10 % sulfuric acid solutions. It was found that the efficiency of *Aloe Vera* extract in a concentration of 0.0800 mg/ml in 10 % sulfuric acid solution was lower about 16 % than in 3 % sodium chloride solution.

The lowest corrosion inhibition efficiency (5.40 %) was observed for as-cast specimens of alloy A exposed to 10 % sulfuric acid solution containing 0.0533 mg/ml of inhibitor. At the same time, the highest efficiency (93.25 %) was ensured for as-cast specimens of alloy A in 3 % sodium chloride solution with a concentration of *Aloe vera* extract of 0.0800 mg/ml.

In addition to the Tafel's linear diagrams, cyclic voltammograms were recorded for each alloy in both media, which further confirmed separation between the anode and cathode peaks. Cyclic voltammetry (CV) represents an easy and fast technique used for characterisation of electrochemical properties of analytes that can be electrochemically oxidised or reduced. The cyclic voltammograms curves can also be used to study the surface coverage of inhibitor molecules. Visible oscillation of current density during a study on corrosion behaviour of 2xxx alloys in 10 % sulfuric acid solutions and 3 % sodium chloride solutions is not beneficial regarding corrosion inhibition. The pitting corrosion appeared due to the dissolution of the oxide film. The negative result of inhibitor addition is observed in an acid medium (0.5 HCl) by Al-Turkustani *et al.*, 2010. The increase in the corrosion rate in the maximal amount of 12.9 % is observed with the addition of a minimum concentration of inhibitor (Al-Turkustani *et al.*, 2010). In our study, the increase in the corrosion rate is recorded for specimens of alloy B exposed to 10 % sulfuric acid solution containing 0.0266 mg/ml of *Aloe Vera* extract. The common inhibitor effect is manifested by shift of the corrosion potential towards more positive side regarding the corrosion potential of medium without inhibitor used. The shift of corrosion potential towards the negative direction with the addition of inhibitor indicates that *Aloe Vera* extract acts as a cathodic inhibitor. Obtained results have shown that *Aloe Vera* extract acts as an activator in the presence of the lowest concentration which could be attributed to the presence of functional groups in the examined extract.

Figure 5 illustrated the cyclic voltammograms of as-cast and heat-treated specimens of alloy B in acid medium. The distinguished oxidation peaks resulted from different conditions of samples prepared from the alloy B. A smaller temperature-dependent corrosion potential can be observed for heat-treated specimens. With the scanning potential ranged from -0.5 V to 0.7 V, the current density of aluminium changed significantly from -0.007 to 0.018 Acm^{-2}. The cyclic voltammogram of the inhibitory reaction to the aluminium alloy in the acid solution of the author Wang et al., shows that the aluminium alloy electrodes in the presence of DAN inhibitor had relatively lower current densities which became lower gradually with the increasing of DAN concentration (Wang *et al.*, 2015). It might be attributed to the adsorption of DAN molecules on the aluminium alloy surface to form the protective layer (Wang *et al.*, 2015).

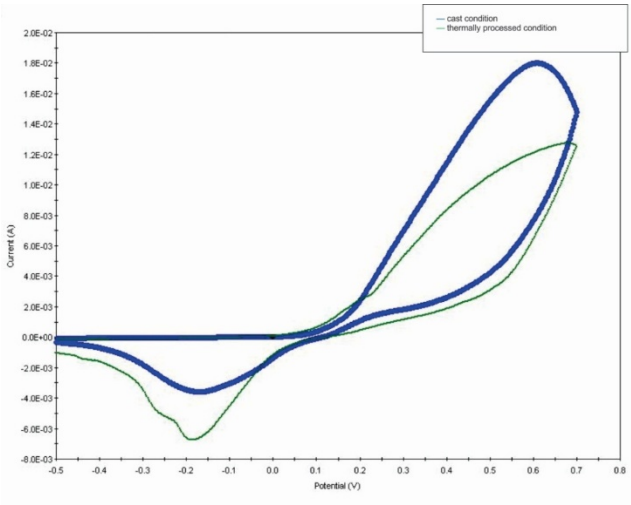

Figure 5. Cyclic voltammogram for as-cast (—) and heat-treated specimens of alloy B (—) in sulfuric acid 10%

CONCLUSION

The inhibitory effects of *Aloe Vera* extract on corrosion of two 2xxx alloys in 10 % sulfuric acid and 3 % sodium chloride solutions were studied. The dependence of the metal dissolving rate on the concentration of inhibitor added in an acid medium was confirmed. The protective film has contained Al^{2+}-*Aloe Vera* complex. Compared to basic solutions, the addition of *Aloe Vera* extract has caused the shift of corrosion potential towards the negative direction for most of the examined samples. Therefore, it has acted as a cathodic inhibitor. However, in the presence of the lowest concentration of *Aloe vera* extract in 10 % sulfuric acid solutions, it has acted as an activator.

Since the influence of *Aloe Vera* extract has changed with increasing concentration in a neutral medium (3 % sodium chloride), it could be used as a corrosion inhibitor with significant inhibition efficiency. The highest efficiency (93.25 %) was ensured for as-cast specimens of the alloy containing 4.78 % of copper and 0.71 % of magnesium in 3 % sodium chloride solution with a concentration of *Aloe vera* extract of 0.08 mg/ml.

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Summary/Sažetak

U ovom radu razmatran je inhibicioni efekat *Aloe vera* na odabrane legure aluminijuma u 10% sumpornoj kiselini i 3% rastvoru natrijum-hlorida na sobnoj temperaturi, korišćenjem metoda potenciodinamičke polarizacije i ciklične voltametrije. Istraživanje je obuhvatilo 2xxx legure kao livene i termički obrađene, sa brzinom skeniranja od 1mV/s za linearnu polarizaciju i 50 mV/s za cikličnu voltametriju. Za svaku ispitivanu leguru primijenjen je različit konstantni potencijal. Rezultati polarizacije ukazuju da se transpasivacija dešava u kiseloj sredini u slučaju svake legure. Dobijeni rezultati pokazuju da ekstrakt *Aloe vere* djeluje kao katodni inhibitor.

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