



BEHAVIOR OF BLACK PEPPER EXTRACT AS A GREEN CORROSION INHIBITOR IN ACIDIC MEDIA

Arlinda Çaçi¹, Jolda Zotaj², Alketa Lame³, Efrosini Kokalari⁴, and Sadik Cenolli

¹PhD student at Faculty of Natural Sciences, University of Tirana, Albania
Avenue Zogu I, Tirana

²PhD student at Faculty of Natural Sciences, University of Tirana, Albania
Avenue Zogu I, Tirana

³Faculty of Natural Sciences, Chemistry Department, University of Tirana, Albania
Avenue Zogu I, Tirana

⁴Faculty of Natural Sciences, Chemistry Department, University of Tirana, Albania
Avenue Zogu I, Tirana

⁵Faculty of Natural Sciences, Chemistry Department, University of Tirana, Albania
Avenue Zogu I, Tirana

Abstract

Corrosion control of metals is of technical, economic, environmental, and aesthetical importance. The use of green inhibitors is one of the best options of protecting metals and alloys against corrosion. Green inhibitors are extracted by plant products. As in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable. We have used Black Pepper extract as a green corrosion inhibitor. Historically, pepper has been thought to cure many illnesses such as cancer, malaria, and cholera; however, today it is most commonly used as a food additive. The material under investigation is Iron B 500 usually applied to concrete as reinforcing bars. The inhibition efficiency of Black Pepper extract in respect of Iron B 500 is investigated in sulphuric acid media in presence of chloride ions, in form of NaCl (1.0 mol/L H₂SO₄ + Cl⁻ 10⁻³ mol/L). Weight loss measurements and an electrochemical method such as potentiodynamic polarization are used for inhibition efficiency testing. Both methods show that inhibition efficiency increases with the increasing concentration of the inhibitors and corrosion rate decreases with the increasing concentration of the inhibitors. Black Pepper extract for weight loss measurements and electrochemical measurements gave respectively 58% and 84% inhibition efficiencies in concentration 1.0 g/L.

Key Words: Black Pepper extract, corrosion, green inhibitors, Iron B 500.

1. Introduction

The studies of iron corrosion in acidic media receive more and more attention both of academics and industrials because of the wide applications. The electrochemical corrosion is generally caused by dissymmetry potentials between metal and strong acid. The aggressiveness of hydrogen ion is inevitable in uninhibited acid. H^+ and Dissolved O_2 are named natural motors of corrosion [1]-[2]. Facing this problem, the corrosion inhibitors are required. Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. Many synthetic compounds offer good anticorrosive action; but most of them risk being highly toxic to both human beings and environment. In these later years, researchers reorient their studies to the use of naturally occurring substances [3].

Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials, and ecologically acceptable. Plant products are organic in nature, and some of the constituents including tannins, organic and amino acids, alkaloids, and pigments are known to exhibit inhibiting action. Moreover, they can be extracted by simple procedures with low cost. Those plant extract are called green inhibitors. Most of the effective inhibitors are used to contain heteroatom such as O, N, and S and multiple bonds in their molecules through which they are adsorbed on the metal surface.

In fact, adsorption process can occur through the replacement of solvent molecules from the metal surface by ions and molecules accumulated near the metal/solution interface. It has been observed that adsorption depends mainly on certain physicochemical properties of the inhibitor group, such as functional groups, electron density at the donor atom, π -orbital character, the electronic structure of the molecule, aromatic rings in their structures, long alkyl chain, etc.

In acidic solutions, transition of the metal/solution interface is attributed to the adsorption of the inhibitor molecules at the metal/solution interface, forming a protective film. The rate of adsorption is usually rapid, and hence, the reactive metal surface is shielded from the acid solutions. The adsorption of an inhibitor depends on its chemical structure, its molecular size, the nature and charged surface of the metal, and distribution of charge over the whole inhibitor molecule. Ions can accumulate at the metal/solution interface in excess of those required to balance the charge on the metal at the operating potential. These ions replace solvent molecules from the metal surface, and their centers reside at the inner Helmholtz plane. This phenomenon is termed specific adsorption, contact adsorption. The anions are adsorbed when the metal surface has an excess positive charge in an amount greater than that required to balance the charge corresponding to the applied potential. The exact nature of the interactions between a metal surface and an aromatic molecule depends on the relative coordinating strength towards the given metal of the particular groups present.

Generally, two modes of adsorption were considered. In one mode, the neutral molecules of leaves extract can be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the heteroatoms and iron. The inhibitor molecules can also adsorb on the mild steel surface based on donor-acceptor interactions between π -electrons of the aromatic/heterocyclic ring and vacant d-orbitals of surface iron. In another mode, since it is well known that the steel surface bears the positive charge in acidic solutions, so it is difficult for the protonated leaves extract to approach the positively charged mild steel surface (H_3O^+ /metal interface) due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, thus they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules, the protonated leaves extract

adsorbed through electrostatic interactions between the positively charged molecules and the negatively charged metal surface.

Since all the different parts of plant extract possess several heteroatoms containing active constituents, therefore there may be a synergism between the molecules accounting for the good inhibition efficiencies [4].

The studies in these years prove that this kind of inhibitor find more and more attention of researchers. In our laboratories, many studies have been investigated on the corrosion inhibition by natural plant extract on mild steel in acidic solutions [5]-[17]. As green corrosion inhibitor we have used Black Pepper extract. In the present work, inhibitive action of Black Pepper extract as a cheap, eco-friendly and naturally occurring substance on corrosion behavior of Iron B 500 (a kind of mild steel) in acidic media (1.0 mol/L H₂SO₄ in presence of chloride ions Cl⁻ 10⁻³ mol/L) has been investigated through weight loss measurements and electrochemical measurements. Black Pepper extract can be extracted in good yield from Black Pepper, which is made up of 5-9% of alkaloids that include piperine, piperidine, piperettine and piperanine (Figure 1) [18].

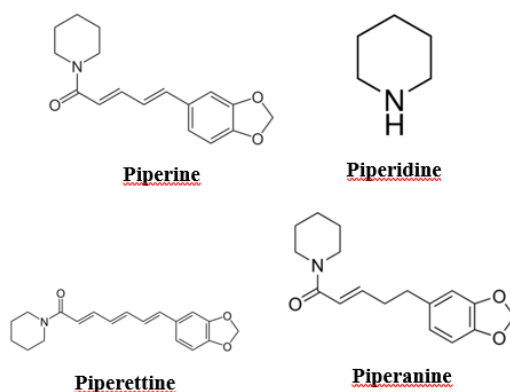


Figure 1: Alkaloids found in Black Pepper

2. Materials and Methods

2.1 Preparation of Black Pepper Extract

Dried Black Pepper seeds (grounds) were crushed and extracted in boiled water for 1 h. The extracted solution was then filtered and concentrated until the water evaporates to half of the initial amount. This extract was used to study the corrosion inhibition properties and to prepare the required concentrations of extracts.

2.2 Specimen Preparation

Iron B 500 specimens having nominal elements composition of 0.224% C, 0.152% Si, 0.680% Mn, 0.110% Cr, 0.102% Ni, 0.318% Cu, 0.021% P, 0.027% S.

2.2.1 Weight Loss Measurements

Samples were cut into cylindrical shape with height 38 mm and diameters 7 mm and 3 mm respectively as shown in Figure 2. The samples were polished using a series of emery paper up to 1200 grade. Then washed thoroughly with deionized water and dried with acetone and with a stream of warm air. The measurements were conducted in 1.0 mol/L sulphuric acid solution in presence of chloride ions Cl⁻ 10⁻³ mol/L, in absence (blanc) and presence of the following extract concentrations: 0.25g/L, 0.5g/L, 0.75g/L and 1g/L. All tests were obtained in deaerated solutions.



Figure 2: Preparation of samples for weight loss measurements

2.2.2 Electrochemical Measurements

Samples are prepared from Iron B 500 in cylindrical shape with diameters 6 mm and 4 mm respectively, and fixed inside a Teflon tube with epoxy resin as shown in Figure 3 [19]-[21]. The measurements were conducted in 1.0 mol/L sulphuric acid solution in presence of chloride ions $\text{Cl}^- 10^{-3}$ mol/L, in absence (blanc) and presence of the following extract concentrations: 0.25g/L, 0.5g/L, 0.75g/L and 1g/L. All tests were obtained in deaerated solutions.

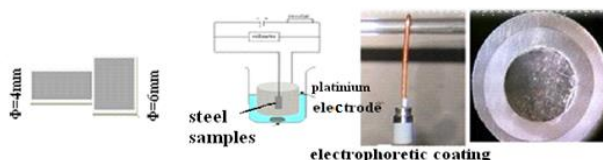


Figure 3: Preparation of samples for electrochemical measurements

2.3 Corrosion Measurements

2.3.1 Weight Loss Measurements

Experiments were performed with different concentrations of the extract and samples were placed in closed glasses container. The immersion time for the weight loss is 24 h at the room temperature.

The corrosion rate (V_{corr}) and inhibition efficiency IE% was calculated using the following equation:

$$V_{corr} \left(\frac{mm}{year} \right) = 8.76 \times \Delta m / (p \times A \times t) \quad (1)$$

Where, in corresponding units Δm the weight difference (mg), p is the density ($p=7.86 \text{ g/cm}^3$), A the surface of the sample (cm^2) and t the time of sample exposure (hours).

$$IE\% = \left(\frac{v_0 - v}{v_0} \right) \times 100 \quad (2)$$

Where, in corresponding units v_0 and v are the corrosion rates of the specimen in 1.0 mol/L sulphuric acid solution in presence of chloride ions $\text{Cl}^- 10^{-3}$ mol/L, in absence (blanc) and presence of extract, respectively.

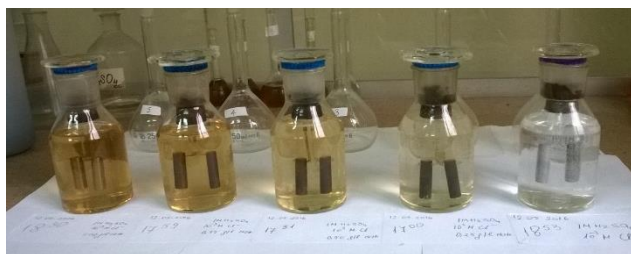


Figure 4: Iron B 500 samples immersed in blanc solution in absence and presence of extract

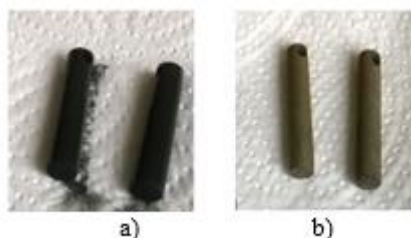


Figure 5: Iron B 500 samples a) with corrosion products (after immersion time), b) after being cleaned by the corrosion products

2.3.2 Electrochemical Measurements

Electrochemical measurements were carried out in a three-electrode electrolysis cylindrical tempered glass cell. Iron B 500, Hg/Hg₂SO₄ electrode and platinum electrode were used as working, reference and auxiliary electrodes, respectively. The polarization curves were recorded with a Potentiostat/Galvanostat/TACUSSEL PJT 24-2 model at a scan rate of 6×10^{-3} V/min [20], [22]. The linear Tafel plots are utilized to provide information about the corrosion rate of Iron B 500 and inhibition efficiency in 1.0 mol/L H₂SO₄ acid solution in presence of chloride ions Cl⁻ 10^{-3} mol/L, in absence (blanc) and presence of the extract. Corrosion current density was determined using the cutting point of Tafel extrapolation line and corrosion rate (V_{corr}) was calculated according to Faraday's law (3) [20]-[23].

$$V_{corr} \left(\frac{mm}{year} \right) = (k * M * i_{corr}) / (n * p) \quad (3)$$

Where, in corresponding units, M is the molar weight of the metal ($M = 56$ g/mol), i_{corr} is corrosion current density, n is the number of electrons exchanged during metal dissolution ($n=2$), p is the density ($p=7.86$ g/cm³) and K is a constant which equals to 0.00327 if corrosion rate (V_{corr}) is calculated in (mm/year) [21].

3. Results and Discussion

3.1 Weight Loss Measurements

The values of percentage inhibition efficiency (% I.E) and corrosion rate by weight loss measurements, in absence (blanc) and presence of Black Pepper extract are summarized in Table I. It was observed that inhibition efficiency increases with increasing concentration of extract and maximum efficiency was observed at 1.0 g/L.

3.2 Electrochemical Measurements

The potentiodynamic polarization curves and the corresponding average Tafel extrapolations are given in Figures 6, 7, 8, 9, 10, 11. The values of corrosion potential, corrosion current density, percentage inhibition efficiency (% I.E) and corrosion rate by electrochemical measurements, in absence (blanc) and presence of Black Pepper extract are summarized in Table II. It was observed that inhibition efficiency increases with increasing concentration of extract and maximum efficiency was observed at 1.0 g/L.

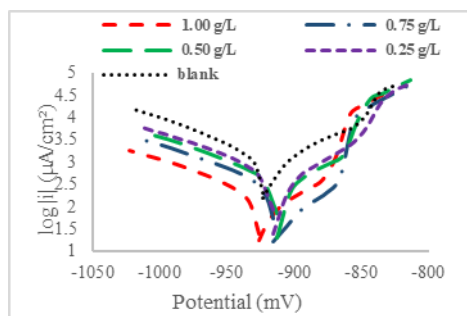


Figure 6: Potentiodynamic polarization curves, in absence and presence of the different concentration of Black Pepper extract

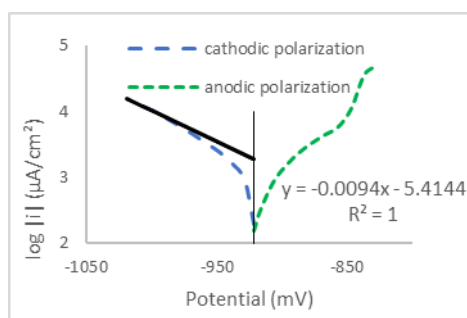


Figure 7: Potentiodynamic polarization curves and Tafel extrapolations, in absence of Black Pepper extract (blanc)

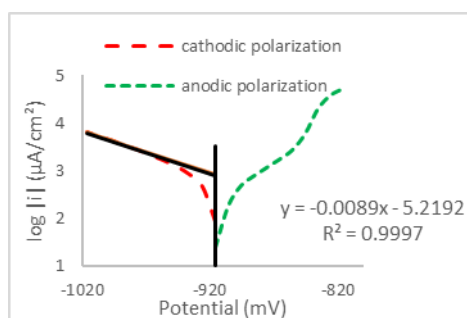


Figure 8: Potentiodynamic polarization curves and Tafel extrapolations, in presence of 0.25 g/L Black Pepper extract

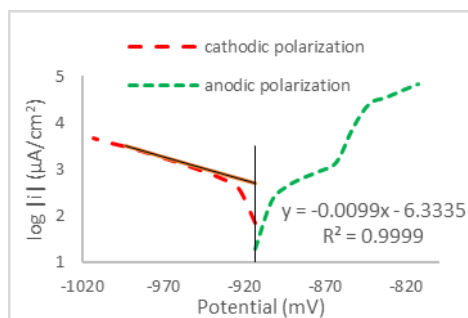


Figure 9: Potentiodynamic polarization curves and Tafel extrapolations, in presence of 0.5 g/L Black Pepper extract

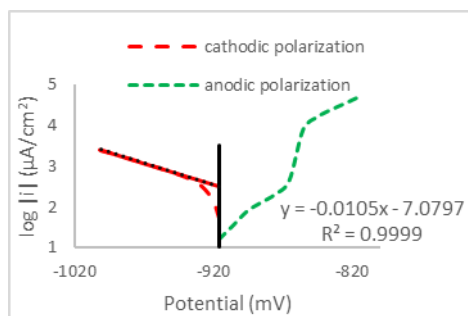


Figure 10: Potentiodynamic polarization curves and Tafel extrapolations, in presence of 0.75 g/L Black Pepper extract

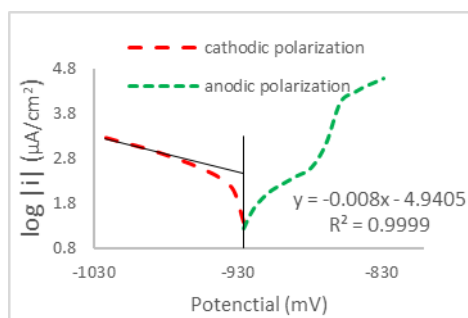


Figure 11: Potentiodynamic polarization curves and Tafel extrapolations, in presence of 1 g/L Black Pepper extract

As we show in all curves it is noticed a regularity of the cathodic polarization branch and an irregularity of the anodic polarization branch, therefore the corrosion current density was determined using the cutting point of Tafel extrapolation line of the cathodic polarization branch [23].

Moreover, the shape of the curves (fig. 6) can justify the barrier film inhibition mechanism, based on the adsorption of the inhibitor on the metal surface, in the case of Iron B 500. Many compounds can form strong bonds with the metallic surface in different ways, like complex formation with a metal ion on the surface or interaction between the π molecular orbitals of the compounds and the d orbital on the metal. The π electron charge density on oxygen atom in presence of acid solution and considerable extent and as a consequence inhibit the corrosion reaction [24].

The corrosion rate and inhibition efficiency for both methods for Iron B 500 in 1.0 mol/L H₂SO₄ acid solution in presence of chloride ions Cl⁻ 10⁻³ mol/L in absence and presence of Black Pepper extract are given in Table I and II. As the Black Pepper extract increases, the corrosion rate decreases.

Table 1: Corrosion rate and inhibition efficiency in absence and presence of black pepper extract

<i>Weight loss measurements</i>		
<i>Extract Concentration (g/L)</i>	<i>Corrosion rate (v) (mm/year)</i>	<i>Inhibition Efficiency IE%</i>
0 (blanc)	88.93	-
0.25	56.82	36.1
0.50	51.74	41.8
0.75	44.88	49.5
1.0	37.34	58

Table 2: Corrosion potential, corrosion current density, corrosion rate and inhibition efficiency in absence and presence of black pepper extract

<i>Electrochemical measurements</i>				
<i>Extract Concentration (g/L)</i>	<i>E_{corr} (mV)</i>	<i>I_{corr} (μA/cm²)</i>	<i>Corrosion rate (v) (mm/year)</i>	<i>Inhibition Efficiency IE%</i>
0 (blanc)	-922	1862.1	21.86	-
0.25	-916	800.9	9.40	57
0.50	-913	498.3	5.85	73.2
0.75	-916	321.8	3.78	82.7
1.0	-926	297.7	3.49	84

As we show in table I and II, inhibition efficiency by weight loss measurements is 58% and by electrochemical measurements is 84%, so there are different values. This can be explained: during the electrochemical measurements the samples are under the influence of external cathodic current. And this behavior may be due to change in the adsorption characteristics of the inhibitor under the influence of the applied cathodic current [25].

In acidic media the inhibitor adsorbed on surface of mild steels by a mechanism called HSAB principle, (hard and soft acids and bases) proposed by Pearson [26]. Soft acids strongly bind soft bases. According to this, mild steels in acid solution acts as soft acids charged positively and compound containing oxygen, acts as soft bases. Adsorption by co-ordinate type linkage through the transfer electron of oxygen atoms to the steel surface gives a stable chelate with ferrous ions. The adsorption of oxygen atoms, forces the molecule to be horizontally oriented at the metal surface, which led to increase the surface coverage and consequently protection efficiency even in the case of low inhibitor concentrations.

This higher inhibitive performance of Black Pepper extract is due to the adsorption of inhibitor at the metal/solution interface, the presence of heteroatoms O and N, the presence of delocalized

π -electrons, the electronic structure of the molecule, aromatic rings in their structures, long alkyl chain, the metal used, environment, etc [4].

It was observed that there is a small shift towards the cathodic region in the values of corrosion potential, which indicates that Black Pepper extract act as a mixed-type inhibitor.

Also the good performance may be attributed to the synergism between the different compounds present in the extracts [4].

4. Conclusions

All measurements showed that the Black Pepper extract has excellent inhibition properties for the corrosion of Iron B 500 in 1.0 mol/L H₂SO₄ acid solution in presence of chloride ions Cl⁻ 10⁻³ mol/L.

The inhibition efficiencies increase with increasing concentration of extract and maximum efficiency was observed at 1.0 g/L.

The inhibition efficiencies determined by weight loss measurements and electrochemical measurements are in good agreement.

Black Pepper extract acts as mixed-type inhibitor.

References

- I.N. Putilova, S.A. Balezin, V.P. Barannik, *Metallic Corrosion Inhibitors*, Pergamon Press, New York, pp 31, 1960.
- M.A. Amin, S.S. Abd El-Rehim, E.E.F. El-Sherbini, R.S. Bayoumi, "The inhibition of low carbon steel corrosion in hydrochloric acid solutions by succinic acid" Part I. Weight loss, polarization, EIS, PZC, EDX and SEM studies, *Electrochim. Acta*, 52, 3588, 2007.
- A.K. Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit, P.V. Rodrigues, "Corrosion inhibition by justicia gendarussa extract in hydrochloric acid solutions", *Corros. Sci.* 51, 2848, 2009.
- S. Ambrish, E. E. Eno, and M. A. Quraishi, "Corrosion Inhibition of Carbon Steel in HCl Solution by Some Plant Extracts", *International Journal of Corrosion*, Volume 2012 Article ID 897430, 20 pages, doi:10.1155/2012/897430, 2012.
- E. Kokalari, A. Lame, B. Kurti, J. Salihila, "The extraction of galactomannan from the endosperms of coffee bean (pretreated with toluene), in order to be used as corrosion inhibitor", *Bulletin of Natural Sciences*, Special issue, ISSN: 224-1779, pp 256-263, 2011.
- E. Kokalari, A. Lame, Xh. Greca, A. Jano, "Extraction of oleuropein from olive leaves, in order to use as inhibitor against the corrosion of metals", *Albanian j. agric. sci. ISSN: 2218-2020*, Special edition, pp 57-60, 2014.
- A. Çaçi, A. Lame, E. Kokalari, J. Zotaj, "Oleuropein as an environmentally friendly inhibitor to corrosion of Iron B 500 in acid media", *The 3rd International Conference on Research and Education – "Challenges Toward the Future" Conference Proceedings, ISSN: 2308-0825*. 23, University of Shkodra "Luigj Gurakuqi", Shkodra, Albania, October 2015.
- E. Kokalari, A. Lame, A. Andoni, A. Jano, "The extraction of biopolymers from the endosperms of some *leguminisaea* plants, in order to be used as corrosion inhibitor", *International Journal of Ecosystems and Ecology Science*, ISSN:2224-4980, vol. 2/3, pp 191-194, September 2012.
- A. Lame, E. Kokalari, A. Jano, "Comparison of corrosion protection efficiency of two kind of polysaccharides extracted by different *leguminosae* plant", *International Journal of Ecosystems and Ecology Science*, ISSN:2224-4980 vol. 2/3, pp 195-200, September 2012.
- A. Jano, A. Lame, E. Kokalari, "Use of extracted green inhibitors as a friendly choice in corrosion protection of lo alloy carbon steel", *Kem. Ind.*61 (11-12), pp 497-503, 2012.

- E. Kokalari, A. Andoni, A. Lame, A. Jano, "Locust bean gum extracted from endosperms of carob tree, a kind of green inhibitors against the corrosion", Proceedings ISBN 978-9928-4011-9-9, International Conference of Ecosystems, pp 600-606, 2012.
- A. Lame, A. Jano, E. Teli, "Sulfuric acid corrosion protection efficiency of locust bean gum for different steels used as concrete armor", Proceedings ISBN 978-9928-4011-9-9, International Conference of Ecosystems, pp 449-455, 2012.
- A. Lame, E. Teli, A. Jano, "Use of green inhibitors for concrete armor protection against H₂SO₄ corrosion", Asian Journal of Chemistry, vol.25, pp 4017-4021, 2013.
- J. Zotaj, A. Çaçi, K. Tare, J. Kokalari, A. Lame, E. Kokalari, "Quercetin extracted from onion skin is an efficient green inhibitor against the corrosion of metals", Albanian Journal Agricultural Sciences, Special edition, ISSN: 2218-2020, April 2017.
- A. Çaçi, A. Lame, E. Kokalari, J. Zotaj, S. Cenolli, "Quercetin as green corrosion inhibitor of Iron B 500", Proceedings of 6-th International Multidisciplinary Conference on New Advanced Methodologies and Techniques in Scientific Research, pp 90-94, vol 1, Ioanina Greece, April 2017.
- J. Zotaj, A. Çaçi, F. Ylli, K. Tare, S. Cenolli, J. Kokalari, A. Lame, E. Kokalari, "Piperine extracted from Black Pepper another appropriate green inhibitor against the corrosion of metals", International Journal of Ecosystems and Ecology Science, vol. 7/4, pp 825-830, October 2017.
- A. Çaçi, A. Lame, E. Kokalari, J. Zotaj, S. Cenolli, "Use of natural plants as green corrosion inhibitors", International Journal of Ecosystems and Ecology Science, vol. 7/4, pp 677-682, October 2017.
- Adapted by L. Grove from Epstein WW, Netz DF, Seidel JL. Isolation of Black Pepper extract from Black Pepper. J Chem Educ; 70: 598-9, 1993.
- M. Abdallah, Portugaliae Electrochimica Acta 22, 161-175, 2004.
- M. G. Fontana, Corrosion Engineering, McGraw-Hill, 1986.
- J. Albana, L. Alketa and K. Efrosini, Ovidus University Annals of Chemistry, accepted for publication, doi: 10.2478/auoc-2014-0002, 2014.
- R. G. Kelly, J. R. Scully, D. W. Shoesmith and R. G. Buchheit, Electrochemical Techniques in Corrosion Science and Engineering, CRC Press, 2002.
- E. Bardal, Engineering Materials and Processes, Corrosion and Protection, Springer- Verlag, 2004.
- I. Thaya Kumar, G. Udayabhanu and N.S. Rawat, (1990), "Plant materials (Azadirachta Indica) as corrosion inhibitor", Proceedings of the 7th European Symposium on Corrosion Inhibitors (7SEIC) Ann. Univ. Ferrara, N. S., Sez. V, Supl. N. 9, vol. 2, pp 735-743, 1990.
- M. N. Desai, P.O. Chauhan and N. Shah, (1990), "Schiff Bases derived from toluidines as corrosion inhibitors for zinc in sulfuric acid solution", Proceedings of the 7th European Symposium on Corrosion Inhibitors (7SEIC) Ann. Univ. Ferrara, N. S., Sez. V, Supl. N. 9, vol. 2, pp 1199-1210, 1990.
- Z. S. Smialowska, "Inhibition of localized corrosion", Proceedings of the 7th European Symposium on Corrosion Inhibitors (7SEIC) Ann. Univ. Ferrara, N. S., Sez. V, Supl. N. 9, vol. 2, pp 979-1001, 1990.

Arlinda Çaçi was born in Berat, Albania on 28th November 1988. She is currently a PhD student in Chemistry at Tirana University, Faculty of Natural Science. She has Master of Science and Bachelor degree in Chemistry from Tirana University, Faculty of Natural Science, Albania in 2012 and 2010 respectively. Her research areas of interest are chemistry and electrochemistry.

Ms. Çaçi works as part time Professor at Polytechnic University of Tirana, Chemistry Department