OLEUROPINE AS AN ENVIRONMENTALLY FRIENDLY INHIBITOR TO CORROSION OF IRON B 500 IN ACID MEDIA

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Abstract

The catastrophic consequences of corrosion in concrete armors and the use of environmentally friendly additives are scientific motivations for our work. The purpose of this study is the use of green inhibitors extracted from various plants as protective additive of armor steel in concrete mud. The material used is iron B500. The Oleuropine inhibitor is extracted from olive leaves with different extraction methods. Oleuropine content in the extract is 17-23% in crude material with 91% purity. The effectiveness of the Oleuropine inhibitor is proven by two methods: the method of weight loss and potentiodynamic polarization method. The environment used is sulfuric acid 1M with chloride ion concentration approximately 10^{-3} in form of NaCl. By the weight loss method, the corrosion rate in (mm/year) and protection efficiency of oleuropine (%) in concentration of 0.75g/l are respectively: 1.64 mm/year and 67.68%. By the potentiodynamic polarization method, the corrosion rate in (mm/year) and protection efficiency of oleuropine (%) in concentration of 0.5g/l are respectively: 0.76 mm/year and 67.52%.

Key words: *concrete armor, corrosion, iron B 500, oleuropine*.

Introduction

Iron B 500 is one of the most widely used engineering materials, despite its relatively limited corrosion resistance. Aqueous solutions of acids are among the most corrosive media (Sastri V, 1997). The use of inhibitor is one of the most practical methods for protecting metals against corrosion and it, in these days, becomes increasingly popular. Most well known acid inhibitors are organic compounds containing nitrogen, sulfur, and oxygen atoms (Ramazan Solmaza, 2011). Nevertheless, the use of chemical inhibitors has been limited because of the environmental threat. In the 21st century, the research in the field of ‘‘green’’ or ‘‘eco-friendly’’ corrosion inhibitors has been addressed toward the goal of using cheap, effective compounds at low or ‘‘zero’’ environmental impact (Sh. Deng, 2012). Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic environment. It is very important to discover inhibitors that protect the environment from corrosive pollution and at the same time are efficient corrosion inhibitors (O. K. Abiola, 2007). In continuation of our work on development of green corrosion inhibitors we have studied the corrosion inhibition behavior of Oleuropine extract (extracted

from olive leaves) on iron B 500 in sulfuric acid 1M with chloride ion concentration approximately 10^{-3} in form of NaCl.

Materials and methods

Materials under investigation is iron B 500. Iron B 500 is manufactured at Elbasan metallurgical plant, intended for concrete armor. The effectiveness of the Oleuropine inhibitor is proven by two methods: the method of weight loss and potentiodynamic polarization method. The samples used for the weight loss method are prepared from iron B 500 in cylindrical shape with diameters 8 mm and 4 mm respectively as shown in Figure 1. The sample are polished with emery paper (250–1000), cleaned with distilled water, dried, degreased with acetone, cleaned with distilled water again, and finally dried. Weigh samples with analytical scales.

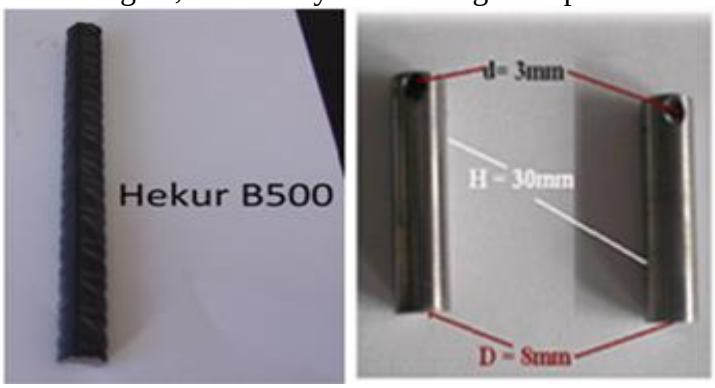
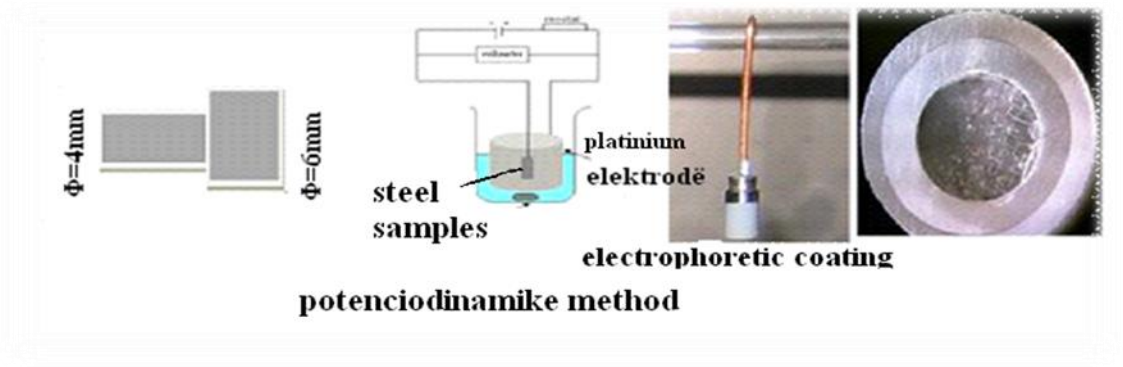


Figure 1–Preparation of samples for weight loss measurements

The samples used for the potentiodynamic measurements 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 2 (M. Abdallah, 2004). For the potentiodynamic measurements the steel samples, before fixed inside the Teflon, were polished with emery paper (250 – 1000), cleaned with distilled water, dried, degreased with acetone, cleaned with distilled water again, and finally dried. To avoid influence of crevice corrosion in electrochemical measurements the samples are pre-coated with electrophoretic coating (M. G. Fontana, 1986).



F i gure 2–Preparation of samples for potentiodynamic polarization measurements

Table 1–Composition of elements for Iron B 500 tested

Elements	C	Si	Mn	Cr	Ni	Cu	P	S
%	0.224	0.152	0.68	0.110	0.102	0.318	0.021	0.027

Media

The corrosion media were prepared with sulfuric acid in the presence of chloride ions, used as blank solutions.

1. The concentration of H_2SO_4 in acidic media is 1 mol L^{-1} and the one of chloride ions is 10^{-3} mol L^{-1} (in the form of NaCl). The pH of solution is about 0.45.
2. As green inhibitor we used oleuropine (Figure 3) extracted from olive leaves with different extraction methods.

Oleuropine is the most abundant phenolic compound in olive leaves .Oleuropine is a heterosidic ester of elenolic deteracid and 3.4 dihydrocyphenylethanol, containing a molecule of glucose, the hydrolysis of which yields elenolic glucoside and hydroxytyrosol (D. Bouknana, 2014).

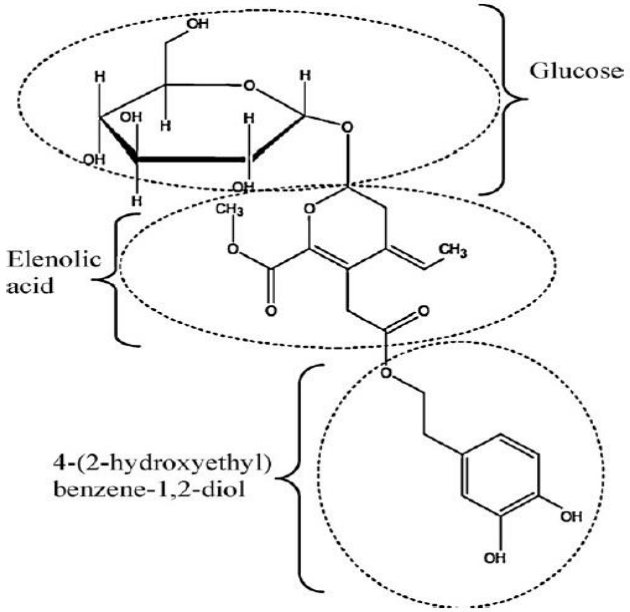


Figure 3–Structures of oleuropein

Table 2–The matrix for weight loss measurements

Nr	Blank	Concentrations of oleuropine extract g L^{-1}		
		0.5	0.75	1
1	+			
2	+			
3	+	+		
4	+		+	
5	+			+

Table 3–The matrix for potentiodynamic polarization measurements

Nr	Blank	Concentrations of oleuropine extract g L^{-1}		
		0.25	0.5	1
1	+			
2	+	+		
3	+		+	
4	+			
5	+			+

Weight loss measurements

By the weight loss method samples were placed in closed glasses container. On the glass container set a stream of pure nitrogen for 30 min inside the solution and above solution for 5 min. Samples were exposed to aggressive environment (1M H_2SO_4+10^{-3} Cl^-) with and without the presence of the inhibitor for 24 hours. Then clean up the surface from corrosion products in a ultrasound bath with a mixture of hydrochloric acid: urotopine (1:1) with concentration of 2g L^{-1}. And finally clean the surface with distilled water, acetone and weight with precision in an analytical scales.

The corrosion rate (υ) and the inhibition efficiency η (%) were calculated from equations (1) and (2):

$$Vcorr(mm/year) = 8.76 \times \Delta m / p \times A \times t \qquad (1)$$

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

$$\eta\ (\%) = (v_0 - v/v_0) * 100 \qquad (2)$$

Where, in corresponding units v_0 and v are the corrosion rates of the specimen in acid solutions without and with the addition of inhibitor, respectively (Gundelia, 2014*)*

Electrochemical measurements

Potentiodynamic measurements were carried out in a typicalthree-electrode electrochemical cell with a Hg/Hg2SO4 electrode as a reference electrode and a platinum electrode as auxiliary electrode. Potentiostat galvanostat type Tacussel PJT 24–2 was used for potenciodynamic measurements. Potential scan rate was $6 \cdot 10^{-3} Vmin^{-1}$ (*Y. Tamaki, 2010*). De-airing of the solution was realized during the potentiodynamic polarization measurements using a stream of pure nitrogen inside the solution for 30 min and above solution for 5 min. Corrosion current density was determined using the cutting point of Tafel extrapolation line and corrosion rate, *V*corr, calculated from equations (3) (*R. G. Kelly, 2002*):

$$Vcorr(mm/year) = k * M * icorr / n * p \qquad (3)$$

Where, in corresponding units, M is the molar weight of the metal (M = 56 gmol–1), icorr is corrosion current density, n is the number of electrons exchanged during metal dissolution (n=2), p is the density (p=7.86 g cm^{-3}) and K is a constant which equals to 0.00327 if corrosion rate (V_{corr}) is calculated in [mm/year].

Results

Weight loss measurements

The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability. Table 4 shows the calculated values of corrosion rates obtained using Eq. (1) as well as inhibition protection efficiency evaluated using the expression given in Eq. (2). The results show that the corrosion efficiencies in each acid medium increased to reach an optimal concentration and corrosion rates decreased to reach an optimal concentration (*E. Bardal*,2004).

- The results are presented in form of corrosion rate (mm/year) and protection efficiency of different additives concentration against corrosion (table 4)

Table 4–Corrosion rate and protection efficiency for iron B 500 in H_2SO_4 1 M and 10^{-3} mol $L^{-1}Cl^-$, pH = 0.45 with and without inhibitor.

Concentrations of oleuropine extract g L^{-1}	IRON B 500	
	V corr	Prot. Effic η %
0 (blank)	5.07	-
0.5	1.75	65.48
0.75	1.64	67.68
1	2.21	56.41

Electrochemical measurements

Results taken by potentiodynamic measurements are given as *V*corr in milimeters per year calculated using corrosion current density (*i*corr). Corrosion current density is determined using the cutting point of Tafel extrapolation line, potentiodynamic polarization curves are given in Figure 4. Figures 5, 6, 7, 8 represents the potentiodynamic polarization curves and the corresponding average Tafel extrapolations line.

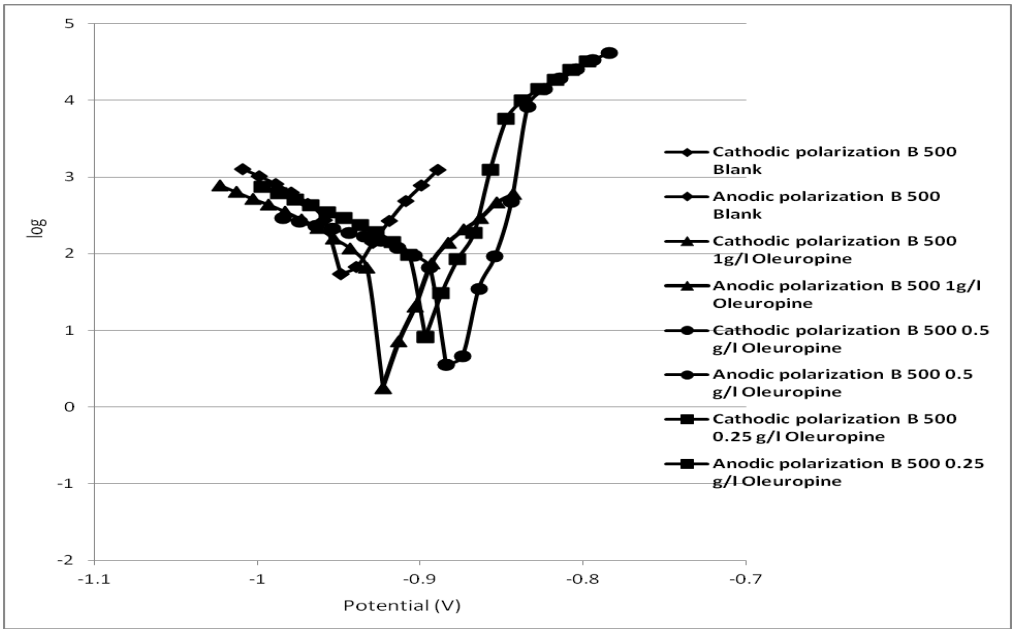


Figure 4–Potentiodynamic polarization curves for iron B 500 *in H_2SO_4 1 mol L^{-1} and 10^{-3} mol $L^{-1}Cl^-$*, pH = 0.45, without and with inhibitor.

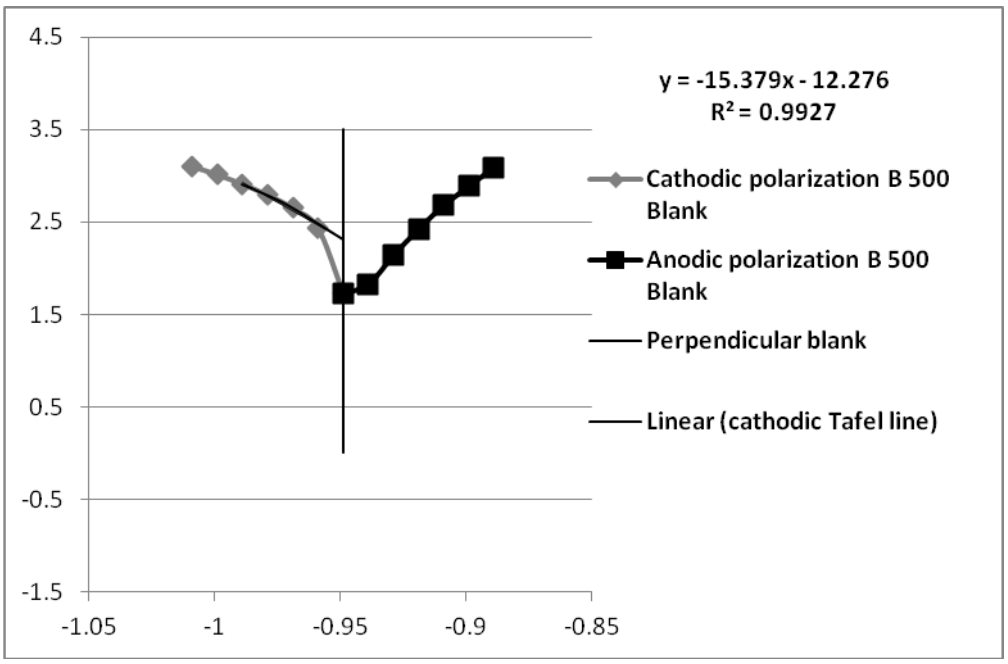


Figure 5–Potentiodynamic curves and Tafel extrapolations for iron B 500 in H_2SO_4 1 mol L^{-1} and 10^{-3} mol $L^{-1}Cl^-$, pH=0.45, without inhibitor.

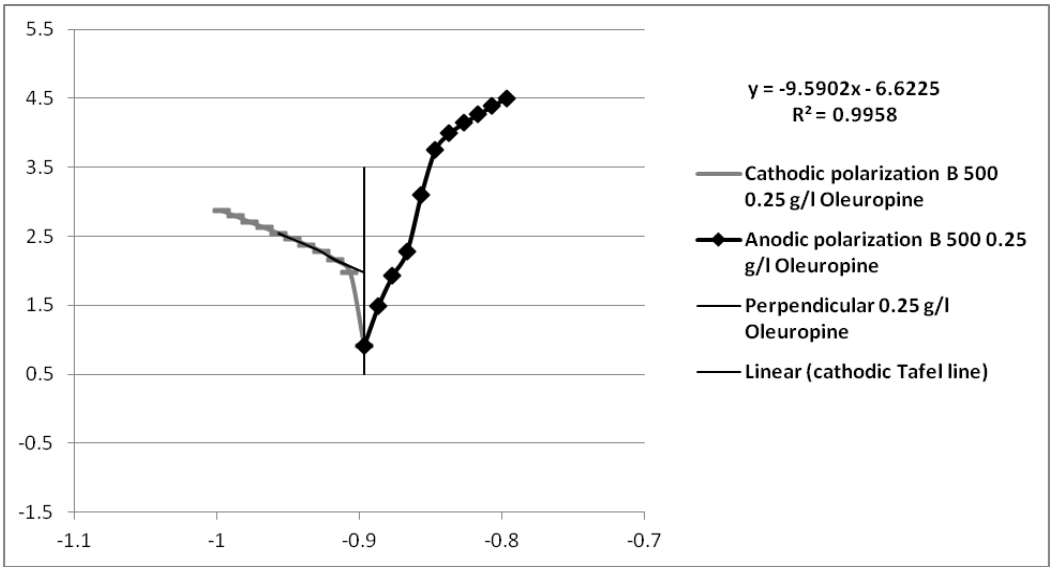


Figure 6–Potentiodynamic curves and Tafel extrapolations for iron B 500 in H_2SO_4 1 mol L^{-1} and 10^{-3} mol $L^{-1}Cl^-$, pH=0.45, in presence of 0.25 g L^{-1} oleuropine extract.

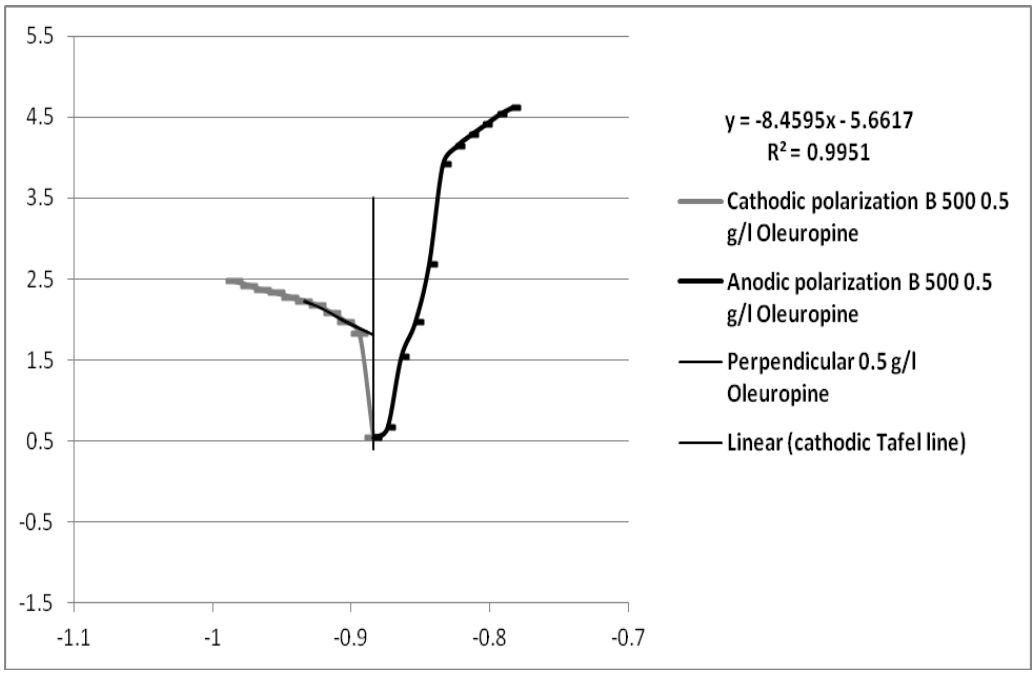


Figure 7–Potentiodynamic curves and Tafel extrapolations for iron B 500 in H_2SO_4 1 mol L^{-1} and 10^{-3} mol $L^{-1}Cl^-$, pH=0.45, in presence of 0.5 g L^{-1} oleuropine extract.

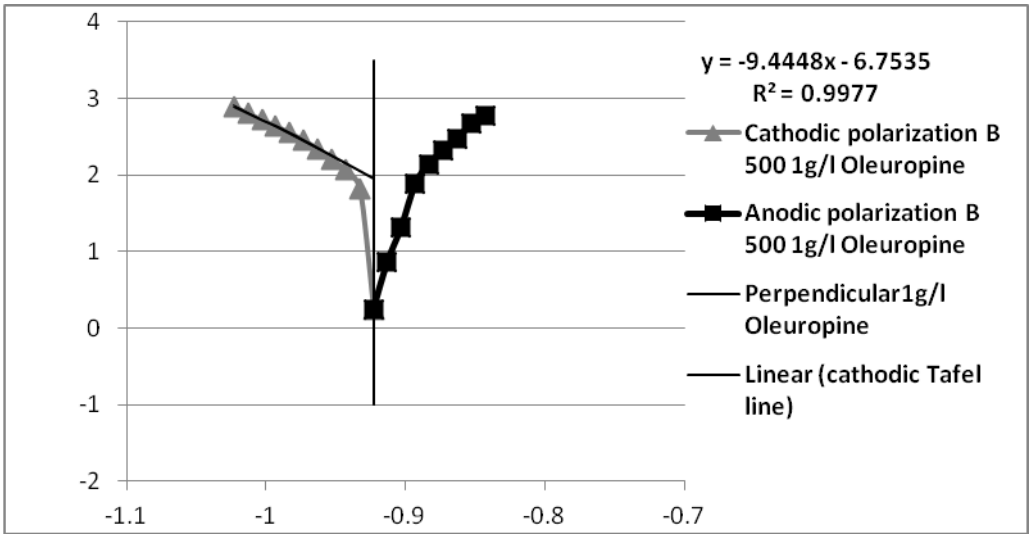


Figure 8–Potentiodynamic curves and Tafel extrapolations for iron B 500 in H_2SO_4 1 mol L^{-1} and 10^{-3} mol $L^{-1}Cl^-$, pH=0.45, in presence of 1 g L^{-1} oleuropine extract.

- The results are presented in form of corrosion rate (mm/year) and protection efficiency of different additives concentration against corrosion (table 5)

Table 5–Corrosion rate and protection efficiency for iron B 500 in H_2SO_4 1 mol L^{-1} and 10^{-3} mol $L^{-1}Cl^-$, pH = 0.45 with and without inhibitor.

Concentrations of oleuropine extract g L^{-1}	IRON B 500	
	V corr	Prot. effic
0 (blank)	2.34	-
0.25	1.11	52.56
0.5	0.76	67.52
1	1.03	55.98

Discussion

Oleuropine extracted by olive leaves adsorbed on surface of iron B 500 by a mechanism called HSAB principle, (*hard and soft acids and bases*) proposed by Pearson. Soft acids strongly bind soft bases. According to this, iron B 500 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. The measurements show that, when the concentration reaches value 0.5g/L the curve represent the higher inhibitor action. For high values concentration (1g/L) the curves are modified. For the concentration higher than 0.5g/L the curves represent the lower inhibitor action. This behavior is attributed to saturation of the

surface by the inhibitor, corresponding to CMC (critical micellar concentration) zone which seems to be near to 0.5g/L. The addition of oleuropine shifts the rest potential of Iron B 500 electrode to more positive values indicating an increased resistance to pitting attack (*S. Varjonen, 2004*).

Conclusions

The measurements for both methods show that, Oleuropine is a good and efficient inhibitor for iron B 500 in 1mol/L H_2SO_4 with 10^{-3}mol/L Cl^- (in form of NaCl).
Inhibition efficiency of iron B 500 in 1mol/L H_2SO_4 with 10^{-3}mol/L Cl^- (in form of NaCl) increased as the concentration of olive leaves extrac increased to reach an optimal concentration.
The concentration 0.5-0.75g/L inhibitor seems to be the CMC, because higher concentrations (1g/L) represent lower inhibitor action.
The use of this extract in the proper concentration as green inhibitor is a smart choice for both: corrosion, and environment protection.

References

D. Bouknana,*a,b* B. Hammouti,*a,c,** M. Messali,*d* A. Aouniti,*a* M. Sbaa, *Portugaliae Electrochimica Acta 2014, 32(1), 1-19 (2014).*
E. Bardal, Engineering Materials and Processes, Corrosion and Protection, Springer-Verlag, London Berlin Heidelberg, 2004, pp. 5–10.
Gundelia tournefortiias a Green Corrosion Inhibitor for Mild Steel in HCl and H2SO4 Solutions, 2014.
M. Abdallah, Guar Gum as Corrosion Inhibitor for Carbon Steel in Sulfuric Acid Solutions, Portugaliae Electrochimica Acta 22 (2004) 161–175.
M. G. Fontana, Corrosion Engineering, 3rd Ed., McGraw-Hill, 1986, pp. 171–174, 153–164, 198–202, 172.
O. K. Abiola, N. C. Oforka, E. E. Ebenso, andN.M.Nwinuka, "Eco-friendly corrosion inhibitors: The inhibitive action of Delonix Regia extract for the corrosion of aluminium in acidic media," *Anti-Corrosion Methods and Materials*, vol. 54, no. 4, pp. 219–224, 2007.
Ramazan Solmaza, EceAltunbas, Gulfeza Kardas, Mater. Chem. Phys.125 (2011) 796–801.
R. G. Kelly, J. R. Scully, D. W. Shoesmith, R. G. Buchheit, Electrochemical Techniques in Corrosion Science and Engineering, CRC Press, 2002, pp. 139–146, 361–371.
Sastri V, Perumareddi JR. Molecular orbital theoretical studies of some organic corrosion inhibitors. Corrosion 1997; 53: 617-22.
S. Varjonen, Accelerated Carbonated Concrete as Corrosion Environment, Nordic Concrete Research 31 (2004) 1–15
Sh. Deng, X. Li, Corros. Sci.55 (2012) 407.
Y. Tamaki, T. Teruya, M. Tako, The Chemical Structure of Galactomannan Isolated from Seeds of *Delonix regia*, Biosci. Biotechnol. Biochem. 74 (5) (2010) 1110–1112.