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Use of Extracted Green Inhibitors as a Friendly Choice in Corrosion Protection of Low Alloy Carbon Steel

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Mitigation of corrosion impact on environment is an important step in environmental protection. Use of environmentally friendly corrosion protection methods is very important. It is smart to choose cheap and safe to handle compounds as corrosion inhibitors. The use of green inhibitors (extracted inexpensively, from the seed endosperm of some Leguminosae plants), and investigation of their efficiency in corrosion protection is the aim of this study. As green inhibitor one kind of polysaccharides (galactomannan) from locust bean gum (also known as carob gum, carob bean gum) extracted from the seed of carob tree is used. Corrosion protection efficiency of these extracted green inhibitors was tested for carbon steel marked as: steel 39, steel 44, and iron B 500 (usually applied as reinforcing bars to concrete). Sulfuric acid solution in the presence of chloride ions was used as corrosion media. The composition of corrosion acid media used was 1 mol L^{-1} H_2SO_4 and 10^{-3} mol L^{-1} Cl^- (in the form of NaCl). Electrochemical techniques such as potentiodynamic polarization methods were used for inhibitor efficiency testing.

Key words: *Green inhibitor, galactomannan, corrosion, carbon steel, linear polarization*

Introduction

Carbon steel is one of the most widely used engineering materials, despite its relatively limited corrosion resistance. Corrosion is one of the main concerns in the durability of metallic materials and their structures. Many efforts have been made to develop a corrosion inhibition process to prolong the life of existing structures and minimize corrosion damages.[1] Corrosion of reinforcing steel in concrete structures, exposed to an acidic media in the presence of chloride ions, is a common occurrence. That is a complex phenomenon related to structural, physical, chemical and environmental considerations.[2] It is well known that concrete is not particularly corrosive for steel bars. The cracks in the concrete, caused by mechanical or chemical stress, are responsible for the penetration of aggressive media (industrial coastal areas) into the reinforced bars. Besides mitigation of chemical and mechanical cracks, the use of green inhibitors, non-toxic substances extracted from plants, will be a friendly choice for both corrosion and environmental protection.

It is very important to discover inhibitors that protect the environment from corrosive pollution and at the same time are efficient corrosion inhibitors.

Our work is based on an earlier publication of *A. Abdallah*,[6] who presents guar – gum as a good inhibitor of acidic environment in the presence of chloride ions. The aim of our scientific motivation has been the use of some substances (a kind of galactomannan) extracted by Leguminosae plants[4,5] as green inhibitor.

Experimental

Materials and methods

Materials under investigation are three marks of low alloy carbon steel respectively steel 39, steel 44 and iron B 500. All materials are manufactured at Elbasan metallurgical plant, intended for concrete armor. The experimental method for investigation of corrosion protection efficiency of extract is electrochemical measurement (potentiodynamic polarization or cyclovoltammetric polarization), where the corrosion current density is used for calculation of corrosion rate. The potentiodynamic measurements are performed with steel 39, steel 44 and iron B500. The samples used for the potentiodynamic measurements are prepared from steel bars in cylindrical shape with diameters 6 mm and 4 mm respectively, and fixed inside a Teflon tube with epoxy resin as shown in Fig. 1.[6,7]

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.[7]

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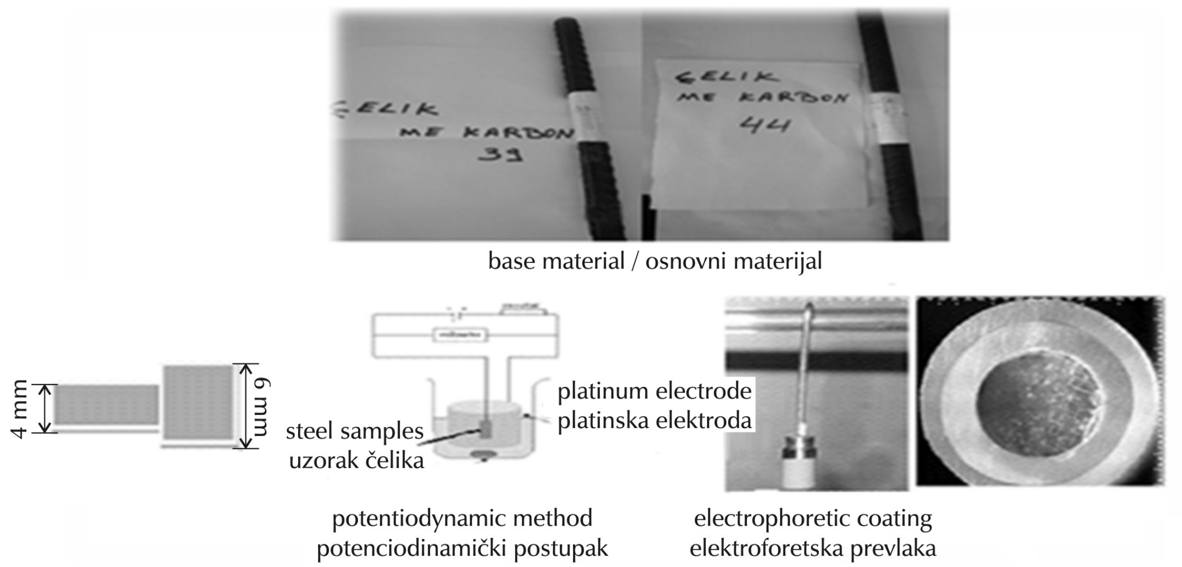


F i g. 1 – *Preparation of samples for potentiodynamic measurements*
S l i k a 1 – *Priprema uzoraka za potenciodinamička ispitivanja*

T a b l e 1 – *Composition of low alloy carbon steel tested*
T a b l i c a 1 – *Sastav ispitivanih uzoraka niskolegiranih ugljičnih čelika*

	w(element) / %							
	C	Si	Mn	Cr	Ni	Cu	P	S
steel 39 čelik 39	0.37	0.17	0.51	0.60	0.60	0.30	0.040	0.040
steel 44 čelik 44	0.445	0.348	0.780	0.118	0.263	0.324	0.0720	0.0440
iron B 500 željezo B 500	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. Two blank solutions have been used.

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 (blank 1).

2. The brine solution (blank 2) with pH ≈ 3.3 – 3.5, realized with blank 1 solution adding sodium hydroxide, NaOH(s). It was used to improve the solubility of locust bean gum in acidic media.

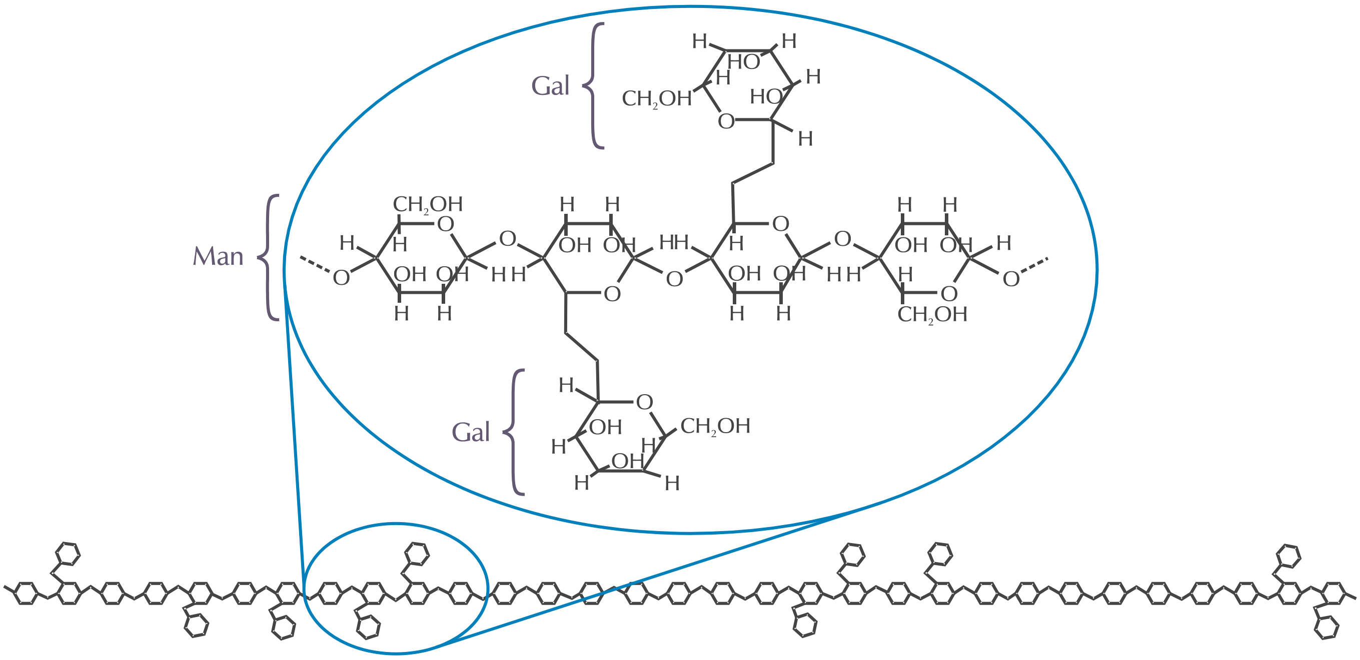
3. As green inhibitor we used a type of polysaccharides (galactomannan) locust bean gum (Fig. 2) extracted from the seed of carob tree at 25 °C followed by precipitation with ethanol.

The solubility of polysaccharides was different by their mannose/galactose (Man/Gal) ratios. In general, the increase of the ratio (Man/Gal) in respect of mannose, decrease the solubility of polysaccharide. In the case of locust bean gum, this ratio is 4/1 (Fig. 2).[8]

The protection affectivity of locust bean gum extracted by endosperms of carob tree was calculated in respect of blank 2 solutions; also the protection affectivity of locust bean gum accompanied with the presence of NaOH was calculated in respect of blank 1 solution.

T a b l e 2 – *Matrix for potenciodynamic measurements*
T a b l i c a 2 – *Pregled potenciodinamička mjerenja*

Nr.	Blank 1	Blank 2	γ(inhibitor) / g L^{-1}		
			0.125	0.25	0.5
1	+				
2		+			
3		+	+		
4		+		+	
5		+			+



F i g. 2 – *Structure of locust bean gum galactomannan (a (1-4)-linked beta-D-mannopyranose backbone with branch points from their 6-positions linked to α-D-galactose, i.e. 1-6-linked α-D-galactopyranose)*

S l i k a 2 – *Struktura galaktomanana iz sjemenke rogača*

Electrochemical measurements

Potentiodynamic measurements were carried out in a typical three-electrode electrochemical cell with an Hg/Hg_2SO_4 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 $3 \cdot 10^{-2}$ V min^{-1}.[7,9] Deaeration of the solution was realized during the potentiodynamic 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 according to Faradays law:[7, 10]

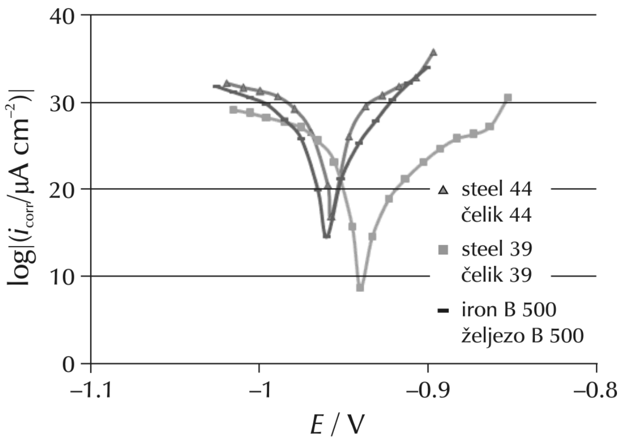
$$\frac{V_{corr}}{\text{mm a}^{-1}} = K \frac{M}{\text{g mol}^{-1}} \frac{i_{corr}}{\text{i A cm}^{-2}} \Big/ n \frac{\rho}{\text{g cm}^{-3}}$$

Where, in corresponding units, M is the molar mass of the metal (M = 56 g mol^{-1}), i_{corr} is corrosion current density, n is the number of electrons exchanged during metal dissolution (n = 2), ρ is the density (ρ = 7.86 g cm^{-3}) and K is a constant which equals 0.00327.

Results and discussion

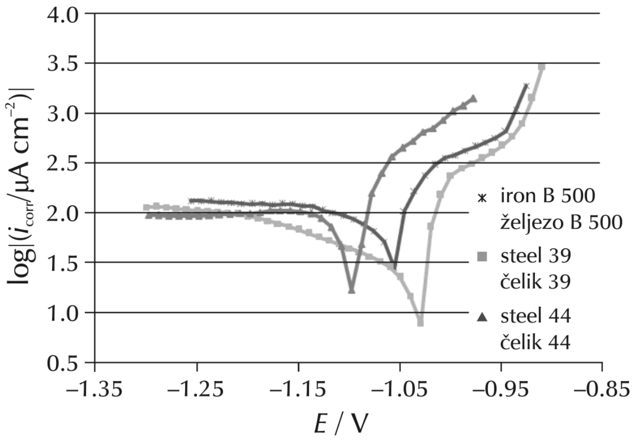
Results taken by potentiodynamic measurements are given as V_{corr} in milimeters per year calculated using corrosion current density (i_{corr}). Corrosion current density is determined using the cutting point of Tafel extrapolation line. Potentiodynamic polarization curves and the corresponding average Tafel extrapolations are given in Figures 3, 4 for steel 39, steel 44, iron B 500 in deaerated solution with $c(H_2SO_4)$ = 1 mol L^{-1} and $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 0.45 without additives referred blank 1 solution, and in deaerated solution with $c(H_2SO_4)$ = 1 mol L^{-1} and $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 3.3 – 3.5, without inhibitor referred blank 2 solution. Figures 5, 6, 7 represent the potentiodynamic polarization curves and the corresponding average Tafel extrapolation line in the presence of 0.5 g L^{-1} locust bean gum extract, in pH = 3.3 – 3.5 for all kinds of low alloy carbon steels under investigation.

In all cases of blank 2 solutions, the rest potential is shifted toward the cathodic potentials. The concentration of SO_4^{2-} ions (in form of Na_2SO_4 salt) in respect to H^+ ions present in



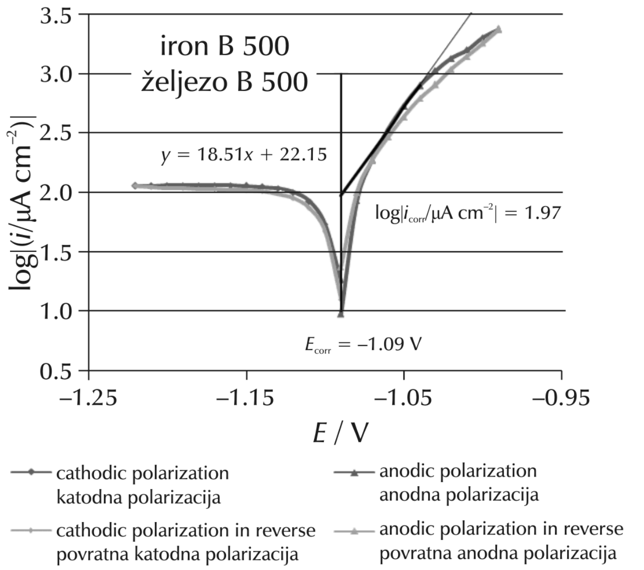
F i g. 3 – *Potentiodynamic polarization curves for steel 44, steel 39, and iron B 500 in deaerated solution with $c(H_2SO_4)$ = 1 mol L^{-1} and $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 0.45, without inhibitor (blank 1)*

S l i k a 3 – *Potenciodinamička polarizacija za čelik 44, čelik 39 i željezo B 500 u odzračenoj otopini bez inhibitora u kojoj je $c(H_2SO_4)$ = 1 mol L^{-1} i $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 0,45 (blank 1)*



F i g. 4 – *Potentiodynamic polarization curves for steel 44, steel 39, and iron B 500 in deaerated solution with $c(H_2SO_4)$ = 1 mol L^{-1} and $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 3.3 – 3.5 without inhibitor (blank 2)*

S l i k a 4 – *Potenciodinamička polarizacija za čelik 44, čelik 39 i željezo B 500 u odzračenoj otopini bez inhibitora u kojoj je $c(H_2SO_4)$ = 1 mol L^{-1} i $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 3,3 – 3,5 (blank 2)*



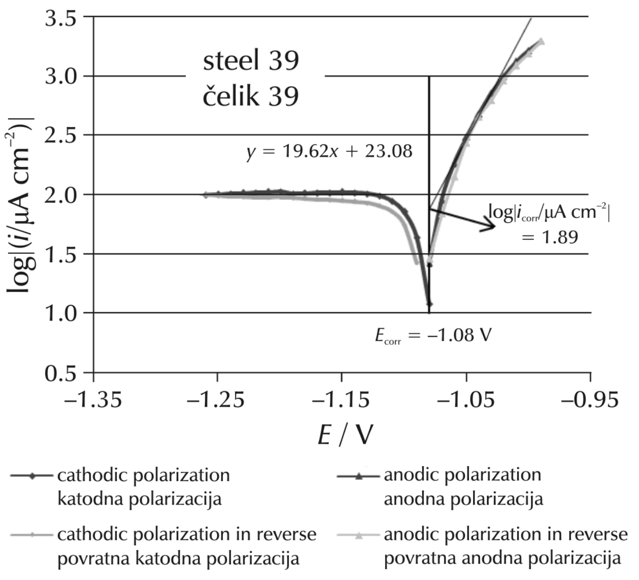
F i g. 6 – *Potentiodynamic curves and Tafel extrapolations for iron B 500 in deaerated solution with $c(H_2SO_4)$ = 1 mol L^{-1} and $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 3.3 – 3.5, in presence of 0.5 g L^{-1} locust bean extract*

S l i k a 6 – *Potenciodinamičke krivulje i ekstrapolirani Tafelovi pravci za željezo B 500 u odzračenoj otopini, $c(H_2SO_4)$ = 1 mol L^{-1}, $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 3,3 – 3,5, uz 0,5 g L^{-1} inhibitora*

blank 2 solution is much higher than in cases of blank 1 solutions. Corrosion in this case, as clearly shown in Fig. 4, depends on concentration polarization.[10] The potential of hydrogen desorption during anodic polarization is clear in both cases (blank 1 and blank 2) of potentiodynamic polarization curves and for all kinds of steel under investigation. The corrosion current density in case of blank 2 solutions was determined as limit cathodic current density (i_L), by cathodic polarization curve.

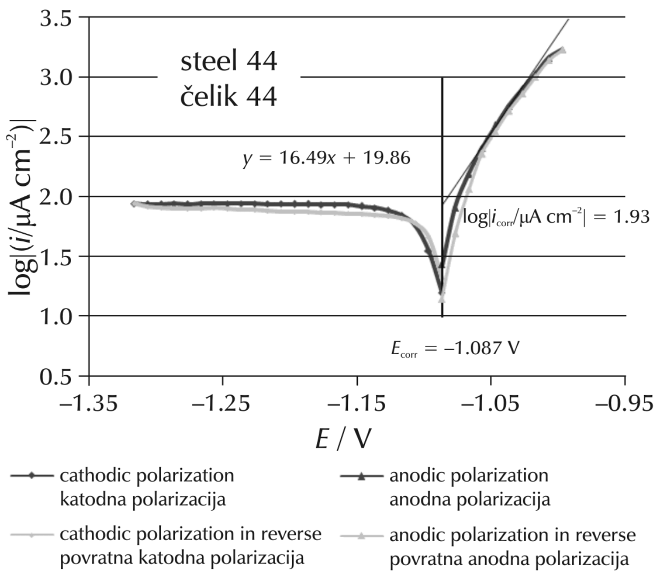
Also, the limit cathodic current density (i_L) in presence of additives is lower than in blank 2 solutions.

From the shapes of the anodic polarization curves in the presence of locust bean gum extract in the anodic polarization region, hydrogen desorption did not occur. The inhibi-



F i g. 5 – *Potentiodynamic curves and Tafel extrapolations for steel 39 in deaerated solution with $c(H_2SO_4)$ = 1 mol L^{-1} and $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 3.3 – 3.5, in presence of 0.5 g L^{-1} locust bean extract*

S l i k a 5 – *Potenciodinamičke krivulje i ekstrapolirani Tafelovi pravci za čelik 39 u odzračenoj otopini, $c(H_2SO_4)$ = 1 mol L^{-1}, $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 3,3 – 3,5, uz 0,5 g L^{-1} inhibitora*



F i g. 7 – *Potentiodynamic curves and Tafel extrapolations for steel 44 in deaerated solution with $c(H_2SO_4)$ = 1 mol L^{-1} and $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 3.3 – 3.5, in presence of 0.5 g L^{-1} locust bean extract*

S l i k a 7 – *Potenciodinamičke krivulje i ekstrapolirani Tafelovi pravci za čelik 44 u odzračenoj otopini, $c(H_2SO_4)$ = 1 mol L^{-1}, $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 3,3 – 3,5, uz 0,5 g L^{-1} inhibitora*

Table 3 – *Corrosion rate and protection efficiency for steel 44, steel 39 and iron B 500 in deaerated solution with $c(H_2SO_4)$ = 1 mol L^{-1} and $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 0.45 (blank 1) and pH = 3.3 – 3.5 (blank 2) with and without inhibitor*[11]

Tablica 3 – *Brzina korozije i djelotvornost zaštite za čelik 44, čelik 39 i željezo B 500 u odzračenoj otopini, $c(H_2SO_4)$ = 1 mol L^{-1}, $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 0,45 (blank 1) i pH = 3,3 – 3,5 (blank 2) s inhibitorom i bez inhibitora*[11]

γ(inhibitor) / g L^{-1}	Mark of steel material Uzorak								
	iron B 500 željezo B 500			steel 39 čelik 39			steel 44 čelik 44		
	V_{corr} / mm a^{-1}	prot. effic. (blank 1) / % djelotv. zaštite (blank 1) / %	prot. effic. (blank 2) / % djelotv. zaštite (blank 2) / %	V_{corr} / mm a^{-1}	prot. effic. (blank 1) / % djelotv. zaštite (blank 1) / %	prot. effic. (blank 2) / % djelotv. zaštite (blank 2) / %	V_{corr} / mm a^{-1}	prot. effic. (blank 1) / % djelotv. zaštite (blank 1) / %	prot. effic. (blank 2) / % djelotv. zaštite (blank 2) / %
0 (blank 1)	6.267	–	–	4.255	–	–	5.602	–	–
0 (blank 2)	2.490	–	–	1.846	–	–	2.292	–	–
0.125	1.664	73.45	33.20	1.209	71.59	34.53	1.380	75.37	39.80
0.25	1.343	78.57	46.07	0.956	77.54	48.23	1.138	79.68	50.34
0.5	1.088	82.64	56.32	0.813	80.89	55.99	0.892	84.08	61.09

tor (like guar gum)[6] was probably adsorbed forming a sustainable chelate with Fe^{2+}, thus blocking the area of hydrogen desorption. Moreover, the anodic reaction of metal is inhibited up to a certain potential, because for more positive potentials, the chelate (formed by Fe^{2+} and inhibitor) may be desorbed. Corrosion rate was evaluated based on the corrosion current density. The determination of corrosion current density is used in the cases where the anodic and the cathodic Tafel line have a cutting point between each other or with the rest potential lines in cases of irregular curves. The results in the form of corrosion rates and protection efficiency of different additives concentration against corrosion are presented in Table 3.

Mass concentration of 0.5 g L^{-1} of locust bean gum extract give the lowest corrosion rates and the highest inhibitor effi-

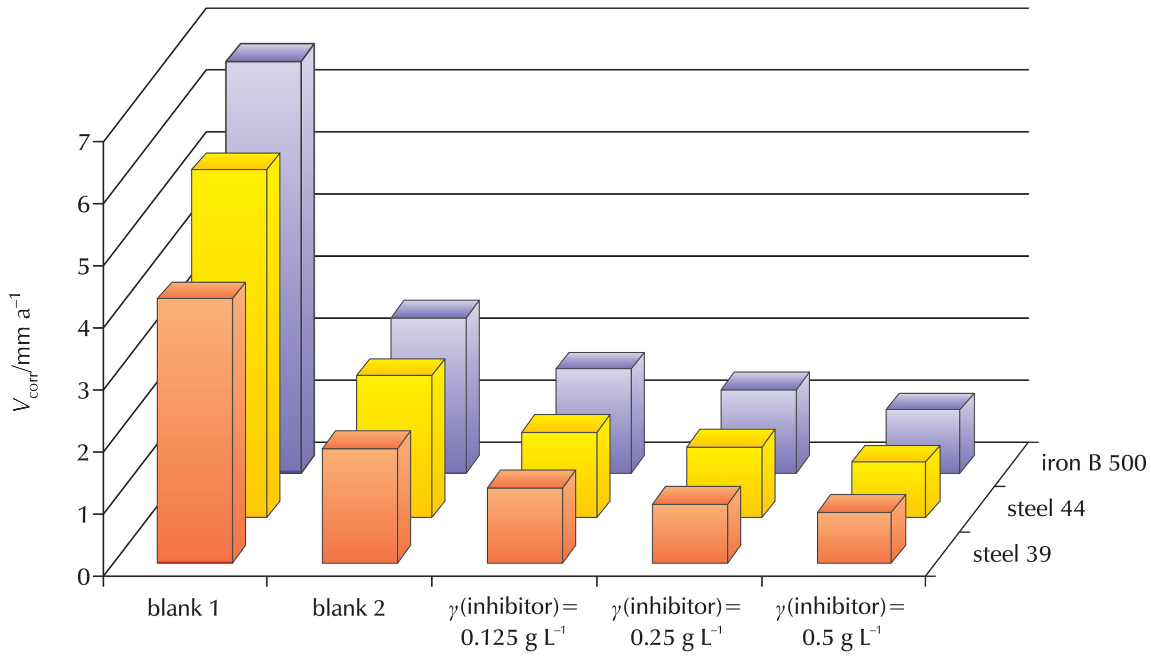


Fig. 8 – *Diagram of corrosion rate for steel 39, steel 44 and iron B 500 in deaerated solution with $c(H_2SO_4)$ = 1 mol L^{-1} and $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 0.45 (blank 1) and pH = 3.3 – 3.5 (blank 2), with and without inhibitor*

Slika 8 – *Brzine korozije za čelik 39, čelik 44 i željezo B 500 u odzračenoj otopini, $c(H_2SO_4)$ = 1 mol L^{-1}, $c(Cl^-)$ = 10^{-3} mol L^{-1}, pH = 0,45 (blank 1) i pH = 3,3 – 3,5 (blank 2), s inhibitorom i bez inhibitora* ciencies (Table 3 and Fig. 8). The protection efficiency referred to blank 2 solutions, in the best case of locust bean gum extract, is not so high: 61.09 % for steel 44 and in concentration 0.5 g L^{-1}. The reasons for this are: on the one hand, the moderate solubility of locust bean gum extract (we used pH 3.3 – 3.5 to improve the solubility value of this one), and on the other hand, the corrosion rate depends on concentration polarisation in this pH value and on the high concentration of SO_4^{2-} and Na^+ ions referred to the hydrogen ions.

Locust bean gum extracted from the carob tree adsorbed on surface of mild steels by a mechanism called HSAB principle, (*hard and soft acids and bases*) proposed by Pearson.[12] Soft acids strongly bind soft bases. According to this, mild steels in acid solution acts as soft acids charged positively and the 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 leads to increased surface coverage and consequently protection efficiency even in the case of low inhibitor concentrations.

Conclusions

Potentiodynamic polarization method showed that: one of the experimental steels (steel 39) presented higher sustainability in the aggressive corrosion media in respect of other steels under investigation.

Steel 39 is recommended for use in aggressive industrial coastal media, such as steel bars for concrete armor. This recommendation is given because the corrosion rate of this steel is the lowest, and exactly 4.255 mm a^{-1} referred to blank 1 solution and 1.846 mm a^{-1} referred to blank 2.

The so-called locust bean galactomannan extracted from carob tree gum mitigates the corrosion rate of the steel 39 from 4.229 mm a^{-1} to 0.81 mm a^{-1} referred to blank 1 solution with protection efficiency 81 %, and from 1.846 mm a^{-1} to 0.81 mm a^{-1} referred to blank 2 solutions with corrosion protection efficiency 56 %.

Finally, we can say that the use of this extract in concentration 0.5 g L^{-1} or more, as green inhibitor supplement in concrete, is a smart choice for both: anticorrosion and environmental protection.

List of symbols and abbreviations
Popis simbola i kratica

c	– amount concentration, mol L^{-1} – množinska koncentracija, mol L^{-1}
E	– potential, V – potencijal, V
E_{corr}	– corrosion potential, V – potencijal korozije, V
i	– current density, μA m^{-2} – gustoća električne struje, μA m^{-2}
i_{corr}	– corrosion current density, μA m^{-2} – gustoća električne struje korozije, μA m^{-2}
i_L	– limit cathodic current density, μA m^{-2} – granična gustoća katodne struje, μA m^{-2}
K	– corrosion rate constant – konstanta brzine korozije
M	– molar mass, g mol^{-1} – molarna masa, g mol^{-1}
n	– number of exchanged electrons – broj izmijenjenih elektrona
V_{corr}	– corrosion rate, mm a^{-1} – brzina korozije, mm a^{-1}
w	– mass fraction, % – maseni udjel, %
γ	– mass concentration, g L^{-1} – masena koncentracija, g L^{-1}
ρ	– density, g cm^{-3} – gustoća, g cm^{-3}
Gal	– galactose – galaktoza
Man	– mannose – manoza

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SAŽETAK

Primjena ekstrahiranih "zelenih" inhibitora pri zaštiti niskolegiranih ugljičnih čelika od korozije

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Ublažavanje utjecaja korozije na okoliš važan je korak u očuvanju okoliša, Posebno se ističu metode zaštite od korozije prihvatljive za okoliš. Treba upotrebljavati jeftine i okolišu prijateljske korozijske inhibitore. To su tzv. zeleni inhibitori. U ovom radu istraživan je inhibitor dobiven iz endosperma sjemena rogača (karuba guma). Djelotvornost u zaštiti od korozije ispitivana je na ugljičnim čelicima (čelik 39 i čelik 44) te željezu B 500. Korozijski medij bio je otopina sumporne kiseline, $c(H_2SO_4) = 1$ mol L^{-1}, čista i uz dodatak i kloridnih iona $c(NaCl) = 10^{-3}$ mol L^{-1}. Primijenjena je elektrokemijska metoda potenciodinamičke polarizacije.

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