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Use of Green Inhibitors for Concrete Armor Protection Against H_2SO_4 Corrosion

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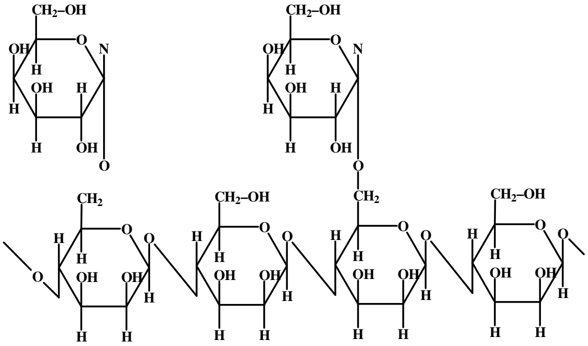
The aim of this study to use the green inhibitors, friendly with environment and investigation of their efficiency in corrosion protection. As green inhibitor, is used one kind of polysaccharide (galactomannan), extracted from the endosperms of some leguminosae plants as coffee beans and chickpeas. Corrosion efficiency of these extracts in sulfuric acid media in presence of chloride ions (blank) was tested for low alloy carbon steels marked as: Steel 39, Steel 44 and iron B-500 (applied to concrete as reinforcing bars). The concentrations of aggressive species are: 1 mol/L H_2SO_4 + 10^{-3} mol/L Cl^- (in form of NaCl). The efficiency of these extracts, at certain concentration (0.75 g/L), against blank, initially was investigated by mass loss measurements. The results compared with protection efficiency of (I^-) ions, which are added in blank as KI with 0.01 mol/L. The electrochemical techniques as potentiodynamic polarization, accompanied with work surface microscope study, are used for optimization of inhibitor concentration. The inhibition action of galactomannan was discussed in terms of its horizontal adsorption.

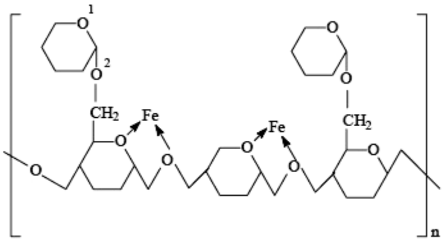
Key Words: Green inhibitor, Galactomannan, Acidic corrosion, Carbon steel.

INTRODUCTION

It is well known that the concrete mud particularly is not corrosive for steel bars. The concrete cracks, are responsible for penetration of aggressive media (industrial coastal areas) into the reinforced bars. Use of corrosion protection methods friendly with environment, is another priority of all scientific opinions related with corrosion sciences. This is very important to choose cheap and safely handled compounds, to be used as corrosion inhibitors. Steel is one of the most important engineering and construction materials in the world. Corrosion problems have received a considerable attention because of their attack on material. Many efforts have been made to develop a corrosion inhibition process to prolong the life of existing structures and minimize corrosion damages[1]. At industrial coastal areas, penetration of the acidic media on steel bars, through chemical or mechanical cracks of concrete, caused corrosion of them[2-6]. Use of inhibitors is one of the most practical methods for corrosion protection. Some inhibitors protect the environment from corrosive pollution, but are unacceptable for it. Beside the mitigation of chemical and mechanical cracks, use of green inhibitors, non-toxic substances (probably extracted by plants), will be a friendly choice for both corrosion and environment protection. Early publication by Abdallah[7] using guar-gum as a good inhibitor of acidic environment in presence of chloride (Cl^-) ions[7]. This has been our scientific motivation for use of same substances (a kind of galactomannan) extracted by leguminosae plants, as corrosion inhibitors for carbon steels bars. The extracts were obtained by aqueous extraction. In order to obtain pure galactomannan, without lipids and proteins the endosperms of these plants were treated first, with toluene: ethanol 2:1 (v/v)[8]. The chemical structure of galactomannans consists of β-(1→4)-D-mannopyranosyl linear backbone, to which α-(1→6)-D-galactopyranosyl simple units are linked, forming short side-branches (Fig. 1a). The presence of hetero oxygen atom in the structure of galactomannan, makes possible its adsorption by co-ordinate type linkage through the transfer of lone pairs of electron of oxygen atoms to the steel surface, giving a stable five membered ring with ferrous ions (Fig. 1b).



(a)



(b)

Fig. 1. Chemical structure of galactomannan (a) and the mechanism of corrosion (b)

EXPERIMENTAL

Materials under investigation are three kinds of low alloy carbon steels, respectively: Steel 39, Steel 44 and iron B 500. All materials were manufactured at Elbasan metallurgical plant, intended for concrete armor. The composition of all the three kinds of low alloy carbon steels are given in Table-1. The experimental method for investigation of corrosion protection efficiency of extracts is weight loss measurement and electrochemical measurement (potentiodynamic polarization or cyclovoltammetric polarization), where the corrosion current density (i_{corr}) is the key for calculation of corrosion rate.

The mass loss experiments were performed with Steel 39 and Steel 44. For weight loss measurements the samples were prepared by cutting of them from steel bars in cylindrical shape with size: (D = 8 mm, H = 30 mm) as shown in Fig. 2.

Fig. 2. Preparation of the samples for weight loss measurements

The working electrodes for potentiodynamic measurements were performed with Steel 39, Steel 44 and iron B500. The samples used for the potentiodynamic measurements were prepared by steel bars (as base material) in cylindrical shape with sizes (D = 6 mm, d = 4 mm) and fixed inside a Teflon tube with epoxy resin[8,9] (Fig. 3). The steel samples, before fixed inside the Teflon, were polished with emery paper (250-1000), cleaned with distilled water, dried, degreased with acetone, cleaned again with distilled water and finally were dried with warm press air. To avoid influence of crevice corrosion in electrochemical measurements the samples are pre-coated with electrophoretic coating[9].

Weight loss measurements: Weight loss experiments carried out in closed glass vessel using a stream of pure nitrogen inside the solution for 0.5 h and above solution for 5 min. Exposure time for weight loss experiment is 24 h. Corrosion rate in (mm/year) is calculated from eqn. 1[10,11]:

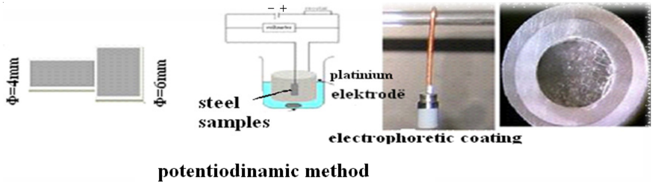


Fig. 3. Preparation of the samples for potentiodynamic measurements

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

where: Δm: the difference of weight in (mg), D : the density in (g/cm^3) (d = 7.86 g/cm^3), A: surface of sample in (cm^2), t: ime of exposure of sample in (hour).

Electrochemical measurements: Potentiodynamic measurements were carried out in a typical three-electrode electrochemical cell with Hg/Hg_2SO_4 *via* a Haber-Luggin capillary as a reference electrode and a platinum electrode as auxiliary electrode. The potentiodynamic measurements were performed with a type PJT 24-1 potentiostat with a potential scanning device. The potencial scan rate is 6×10^{-3} V/min[9,11].

Corrosion current density was determined using the cutting point of Tafel extrapolation line (cathodic and anodic Tafel line) and Faradays law, eqn. 2[10,11]:

$$V_{corr} = \frac{(K \times a \times i)}{(n \times D)} \quad (2)$$

where: a: is the atomic weight of the metal (a = 56 g/mol for Fe), i: the current density in (μA/cm^2), n: the number of electrons exchanged during metal dissolution (n = 2), D: the density in g/cm^3 (D = 7.86 g/cm^3) and K: is a constant, which is equals to 0.00327 if corrosion rate (V_{corr}) is calculated in (mm/y).

Pre-treatment of the working electrode surfaces: (a) Wet grinding subsequently with 120, 240, 320, 600, 1000 grade emery paper. (b) Rinsing with distilled water. (c) Drying with warm pressurized air. (d) Degreasing subsequently with petrolether, acetone and methanol. (e) Rinsing with distilled water and drying with warm oil-free pressurized air.

After each electrochemical measurement the working electrode was treated with a solution of HCl (1:1) + 2 g/L hexamethylenediamine.

Media: The aggressive corrosion media consists in sulfuric acid in presence of chloride ions, imitating the aggressive coastal atmosphere.

The concentration of acidic media is 1 mol/L H_2SO_4 and the one of chloride ions is 10^{-3} mol/L (in form of NaCl)[8]. The pH of blank solution is about 0.45.

The composition of solutions for investigation of different extracts taken by different ways with weight loss measurements, referred low alloy carbon steel St. 44 are as in matrix of Table-2.

The matrix of green inhibitor concentrations (green coffee beans extract, pre selected by mass loss measurements) for potentiodynamic measurements referred steel 39, steel 44 and iron B 500 is as in Table-3.

TABLE-1
COMPOSITIONS OF LOW ALLOY CARBON STEELS TESTED

Element (mass %)	C	Si	Mn	Cr	Ni	Cu	P	S
Steel 39	0.370	0.170	0.510	0.600	0.600	0.300	0.040	0.040
Steel 44	0.445	0.348	0.780	0.118	0.263	0.324	0.072	0.044
Iron B 500	0.224	0.152	0.680	0.110	0.102	0.318	0.021	0.027

TABLE-2
COMPOSITIONS OF SOLUTIONS FOR WEIGHT LOSS MEASUREMENTS

Nr. tests	Blank	I^- 0.01 (mol/L)	Green coffee beans extract (0.75 g/L)		Chickpeas extract (0.75 g/L)	
			With water	With toluene	With water	With toluene
1	+	–	–	–	–	–
2	+	+	–	–	–	–
3	+	–	+	–	–	–
4	+	–	–	+	–	–
5	+	–	–	–	+	–
6	+	–	–	–	–	+

TABLE-3
COMPOSITIONS OF SOLUTIONS FOR POTENTIODYNAMIC MEASUREMENTS

No. tests	Blank	Concentrations of green coffee beans extract (g/L)			
		0.25	0.5	0.75	1
1	+	–	–	–	–
2	–	+	–	–	–
3	–	–	+	–	–
4	–	–	–	+	–
5	–	–	–	–	+

All experiments were run at room temperature under stagnant conditions. The samples were visually and microscopically (stereomicroscope NEOPHOT 21) inspected after the test runs.

RESULTS AND DISCUSSION

Weight loss measurement: The results of weight loss measurements for corrosion rate and protection efficiency of green coffee beans and chickpeas extracted with water or toluene, referred blank solution, compared with protection efficiency of (I^-) ions (0.01 mol/L), are given in Table-4 and Fig. 4. The aim of weigh loss measurements is the pre-selection of the best extract referred corrosion protection in order to use as green inhibitor for steel bars under investigation, during potentiodynamic measurements. The results in Table-4 are given in respect of one kind of low allow carbon steels under investigation (St. 44).

Table-4 (Fig. 4) designed by weight loss measurements data, show that the extract taken by green coffee beans, extracted with toluene is more protective for steel 44 again corrosion in acidic media in presence of chloride ions, compared with extracts taken by chickpeas in both methods (with water and with toluene). The protection efficiency in this case (0.75 g/L the concentration of additive) is almost 99 %. By comparing the corrosion rates and protection efficiencies in Fig. 4 and Table-4, it can be seen that the inhibitive properties of KI in molar sulfuric acid in presence of chloride ions are in general good[11] (related with its low concentration 0.01 mol/L). Corrosion rate and protection efficiency in this case are, respectively 0.661 mm/year and 89.75 %. According to the hard soft acid base principle, the I^- ions as weak base, adsorbed on the surface of carbon steel as weak acid in acidic media[12]. Probably, use of iodide ions (even in low concentration) can increase the degree of surface coverage by extracts with moderate solubility, completing the uncovered surfaces of the carbon steel.

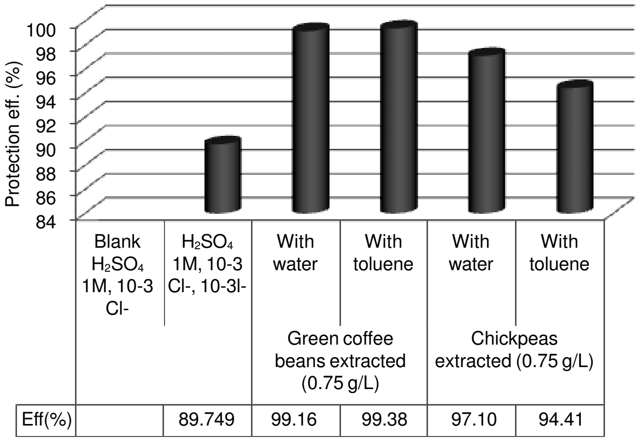


Fig. 4. Diagram of corrosion protection efficiency in %, for different extracts taken by different extractions way, compared with one of the iodine ions

Potentiodynamic polarization: Results taken by potentiodynamic measurements are given in form of V_{corr} in (mm/year). Corrosion rate was evaluated by corrosion current density. (i_{corr}). The anodic, cathodic tafel line and cutting point of them with each - other or with rest potential line, in case of irregular curves, were used for determination of corrosion current density. Potentiodynamic polarization curves and the corresponding average tafel extrapolations are given in Figs. 5-8 for steel 39, steel 44 and iron B 500 in de-aerated 1 M H_2SO_4 solution, 10^{-3} M chloride ions without additives (blank) and in presence of 1 g/L coffee beans extract (the concentration with best protection result).

Potentiodynamic polarization curves for three kinds of steels under investigation St. 44; St. 39 and iron B 500, as

TABLE-4
CORROSION RATE AND PROTECTION EFFICIENCY OF GREEN COFFEE BEANS AND CHICKPEAS EXTRACTS, TAKEN BY TWO DIFFERENT WAYS, IN 1 M H_2SO_4 SOLUTION IN PRESENCE OF 10^{-3} Cl^- (BLANK) COMPARED WITH ONE OF 10^{-2} I^- IONS

Media	Concentration (mol/L)		Green coffee beans extracted (0.75 g/L)		Chickpeas extracted (0.75 g/L)	
	Blank) 1 M H_2SO_4 + Cl^- (10^{-3})	Blank + I^- (10^{-2})	With water	With toluene	With water	With toluene
V_{corr} (mm/year)	6.452	0.661	0.054	0.04	0.187	0.361
Prot. eff. (%)	–	89.749	99.160	99.38	97.100	94.410

clearly shows in Fig. 5, presents steel 39 as more sustainable again corrosion in blank solution (more aggressive acidic media). The branch of polarizations curves for steel 39 are below the curves of other steels (Steel 44 and iron B 500) and the corrosion potential shift towards more positive values. That main: the oxide surface layer for Steel 39, in these aggressive conditions, is more protective then at the other steels under investigations. The corrosion current density determinations, for all steels under investigations in blank conditions, were evaluated as in case of irregular anodic polarization curves (*e.g.*, in this case according to regular anodic polarization curves).

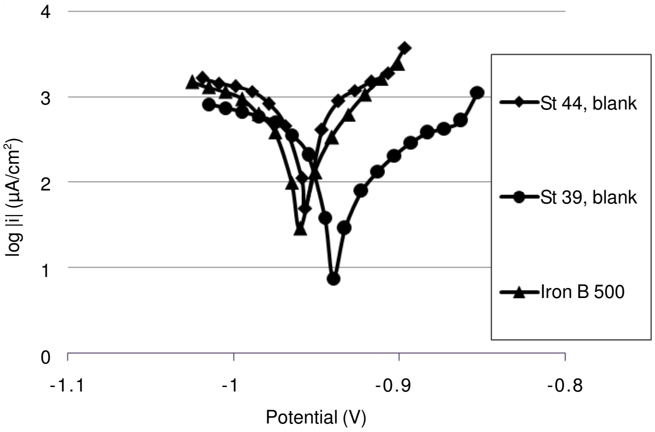


Fig. 5. Potentiodynamic polarization curves for St. 44; St. 39 and iron B 500 in de-aerated 1 M H_2SO_4 solution with 10^{-3} M Cl^-, without additives (blank solution)

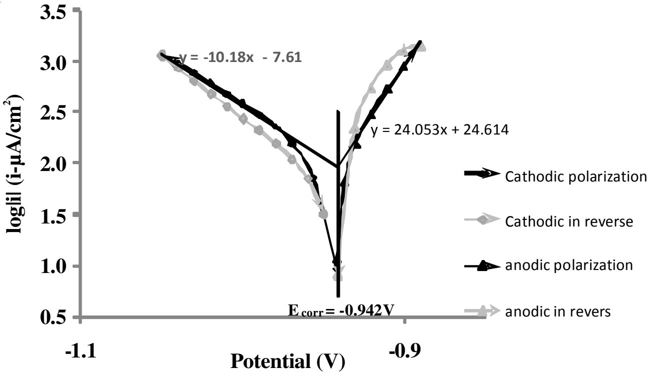


Fig. 6. Potentiodynamic polarization curves and tafel extrapolations for St. 44 in de-aerated 1 M H_2SO_4 solution with 10^{-3} M Cl^-, in presence of 1 g/L of coffee beans extract

For all steels under investigations, except St. 39, the potentiodynamic polarization curves (anodic and cathodic), in presence of green coffee beans extract (green inhibitor), have a regular shape. The corrosion current densities are determined by cutting point of anodic and cathodic tafel extrapolated lines with each-other. The hysteresis for cathodic cyclic polarization curves, as seen to be in comparative manner by Figs. 6-8, show that the smallest adsorption for H_2 occurs at steel 39 in respect of other steels. On the other hand, that means, the good adsorption of additive on the surface of electrode.

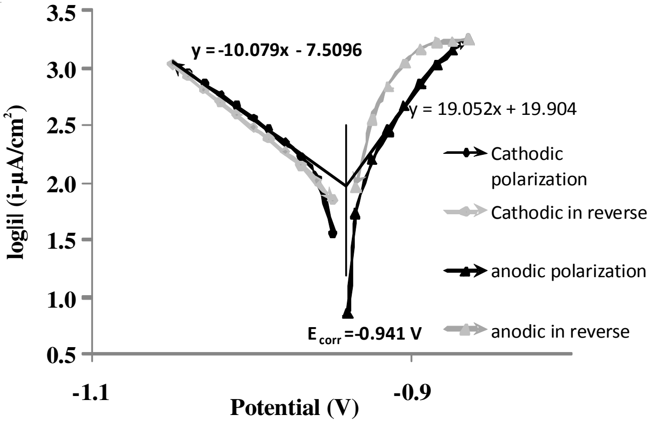


Fig. 7. Potentiodynamic polarization curves and tafel extrapolations for iron B500 in de-aerated 1 M H_2SO_4 solution with 10^{-3} M Cl^-, in presence of 1 g/L coffee beans extract

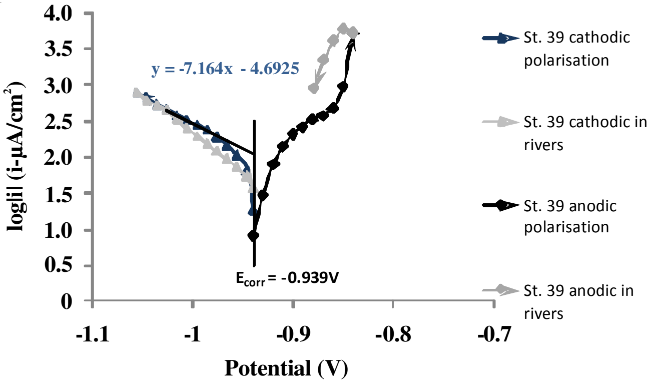


Fig. 8. Potentiodynamic polarization curves and anodic tafel extrapolation for St. 39 in de-aerated 1 M H_2SO_4 solution with 10^{-3} M Cl^- in presence of 1 g/L coffee beans extract

Table-5 (Fig. 9) shows that the increased of additive concentration decreased the corrosion rate. The use of 1 g/L concentration coffee beans extracts lead to the lowest corrosion rates and the highest inhibitor efficiencies, in all low alloy carbon steels under investigations destined for bars. This was also confirmed by visual and microscopic inspection of the electrode surfaces after the experiments (Fig. 10).

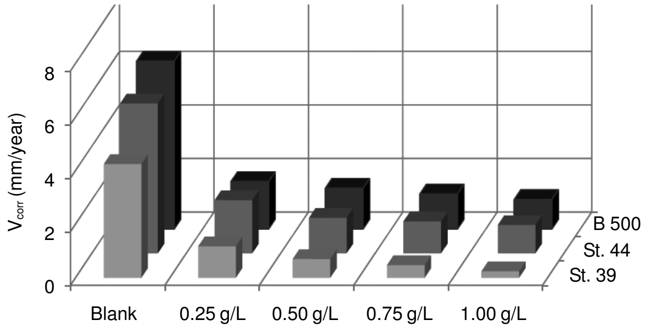


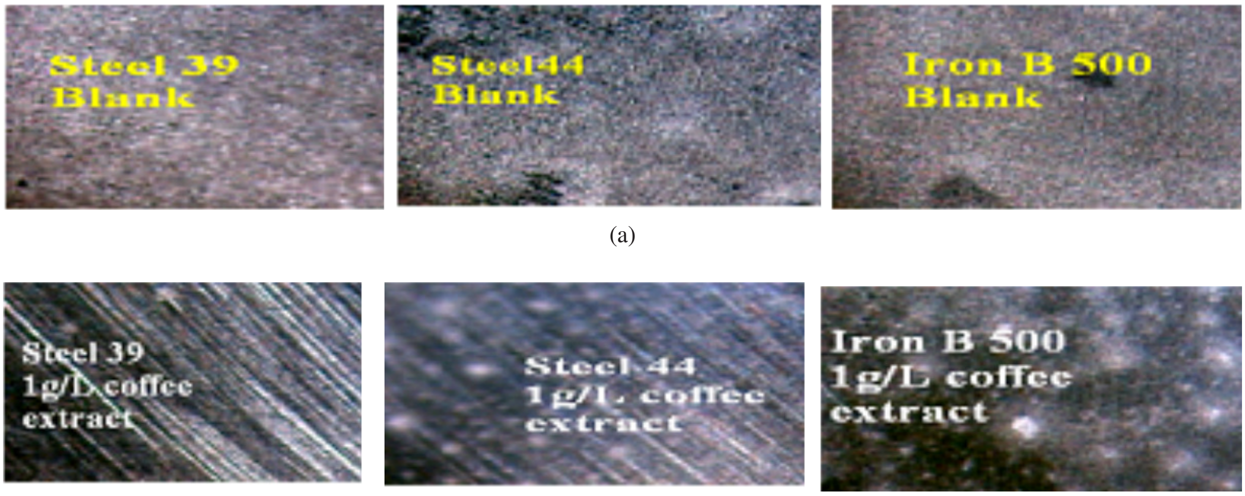
Fig. 9. Diagram of corrosion rate for St. 39, St. 44 and iron B500 in de-aerated 1 M H_2SO_4 solution, 10^{-3} Cl^-, with and without additives

Conclusion

Weight loss methods show that the acetonic extract of green coffee beans presents the better corrosion protection efficiency for three kinds of low alloy carbon steels bars in H_2SO_4 media and in presence of Cl^- ions (Table-4, Fig. 4).

TABLE-5
CORROSION RATE AND PROTECTION EFFICIENCY FOR St.44, St.39 AND B500 IN DE-AERATED 1 M H_2SO_4 SOLUTION WITH 10^{-3} M Cl^-, WITH AND WITHOUT ADDITIVES[9]

Conc. of extract	0.25 g/L		0.5 g/L		0.75 g/L		1 g/L		Blank
Mark of steel	Eff. (%)	V_{corr} (mm/year)	Eff (%)	V_{corr} (mm/year)	Eff (%)	V_{corr} (mm/year)	Eff (%)	V_{corr} (mm/year)	V_{corr} (mm/year)
B500	71.75	1.770	75.73	1.521	79.15	1.307	82.43	1.101	6.267
Steel 39	72.28	1.180	83.41	0.706	88.78	0.477	94.10	0.251	4.255
Steel 44	64.47	1.991	76.19	1.334	78.63	1.197	81.02	1.063	5.602



(a)

(b)

Fig. 10. Surface views of working electrodes after potentiodynamic measurements: (a) St. 39, St. 44 and B500 in de-aerated 1 M H_2SO_4 solution, 10^{-3} Cl^- (blank) and (b) St.39, St44 and B500 in de-aerated 1 M H_2SO_4 solution, 10^{-3} Cl^- in presence of 1 g/L coffee beans extract

Potentiodynamic polarization method (Fig. 5) shows that one of the experimental steels, exactly St. 39, presents higher sustainability again corrosion in this aggressive media. Steel 39 recommended for use in such aggressive industrial coastal media, as steel bars for concrete armor because the corrosion rate for it is the lowest, exactly 4.255 mm/year and it is very sensitive *versus* presence of inhibitor. The corrosion rate decrease approximately 20 times. Galactomannan extracted by green coffee beans mitigate the corrosion rate for Steel 39 from: 4.229-0.251 mm/year with corrosion protection efficiency 94.1 %. In this case the corrosion resistance was classified as good, in respect of aggressive conditions of environment (industrial coastal atmosphere)[11]. The extraction of galactomannan adsorbed initially by hard-soft acid-base principle[13] (hetero oxygen's, as a weak bases, transformed lone pairs of electrons to steel surface as a weak acid) and after formed a stable chelat with Fe^{2+}. Finally, use in concentration 1 g/L of this extract, as green inhibitor supplement, in concrete, is a smart choice for both corrosion and environment protection.

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