Investigation of Citronella Oil as Green Corrosion Inhibitor for Carbon Steel in Corrosive Media

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Introduction

The aim of this study is to investigate the corrosion inhibition of the Carbon steel in 3.5 wt.% NaCl solution, as simulated seawater, containing Citronella oil extract. The eco-friendly inhibitor, Citronella oil extract, was evaluated for corrosion inhibition action by a set of electrochemical experiments: Open Circuit Potential (OCP) measurements, Tafel plots and Electrochemical Impedance Spectroscopy (EIS) [1]. Atomic Force Microscopy (AFM) has been used to analyze the topography surface characteristics of the unmodified and modified electrodes based on Carbon steel. Also, the surface evaluation of the Carbon steel specimens subjected to the inhibitor loaded solution was examined by SEM and EDS [2].

Experimental

The corrosion tests were realized in a conventional **three electrode** cell which contains: carbon steel with flat shape as *working electrode* (S = 2 cm^2), Ag/AgCl,KClsat. as *reference electrode* and platinum wire as *counter electrode*.

Green Inhibitor: citronella oil (C. oil).

Electrochemical experiments were performed using an Autolab (306N Methrom) and started with measuring the potential of the working electrode in an open circuit for 1 hour. To determine the polarization resistance of the electrodes, linear polarization curves were recorded in acidic and chloride containing solutions: HCl 0.1M and NaCl 3.5 wt.% in a potential domain of ± 20 mV *vs.* OCP value To determine the kinetic parameters of the corrosion process, polarization curves were recorded in the potential range of ± 200 mV *vs.* OCP (Fig. 1). EIS measurements were carried out in a frequency range from 10 mHz to 100 kHz at 10 points/decade, AC voltage amplitude of ± 10 mV. The impedance data were interpreted on the basis of equivalent electrical circuits, using the ZSimpWin V3.21 software for fitting the experimental data. The quality of fitting proced2ure was evaluated by the chi squared (χ) values, which were of order 10^{-4}.

Results and discussion

Electrochemical measurements: The polarization resistance values for each electrode, calculated as the inverse of the slope of each curve, are shown in Table 1.

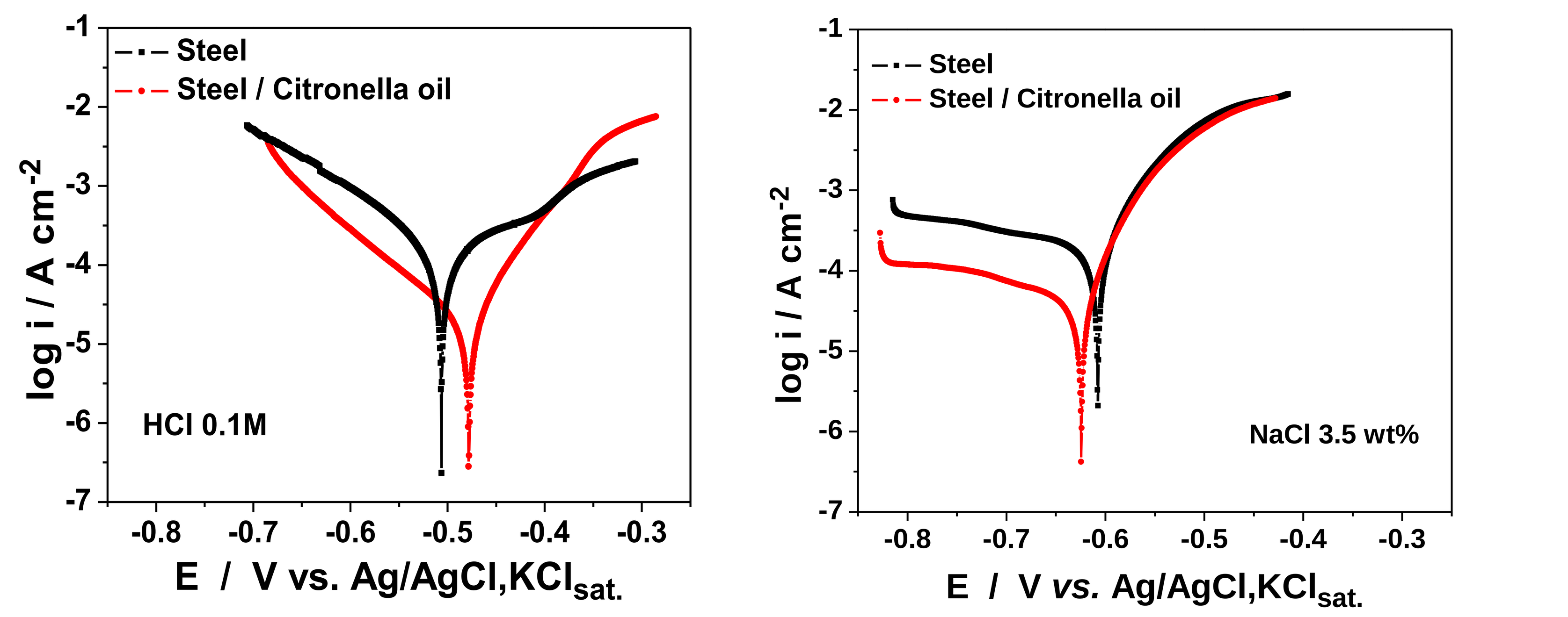

Fig. 1. *The polarization curves (± 200 mV vs. OCP) for the studied electrodes immersed in corrosive solution: HCl 0.1M (left) and NaCl 3.5 wt.% (right).*

Table 1. *Corrosion process parameters for the examined samples*

Corrosion solution	Inhibitor	E_{corr} [mV]	i_{corr} [μA/cm^2]	-βc [mV]	βa [mV]	R_p [Ω*cm^2]	v_{corr} (mm/year)	PE [%]
HCl 0.1M	-	-507	94.2	45	51	2,6	2.55	-
	Citronella oil	-486	75.3	49	38	10.6	1.39	75.5
NaCl 3.5 wt.%	-	- 608	137	55	29	5,3	2.04	-
	Citronella oil	- 624	25	39	20	27	0.37	80.4

The protection efficiency of the inhibitor was determined according to the relation: $PE[\%] = \frac{R_p inhibitor - R_{p0}}{R_p inhibitor} x100$

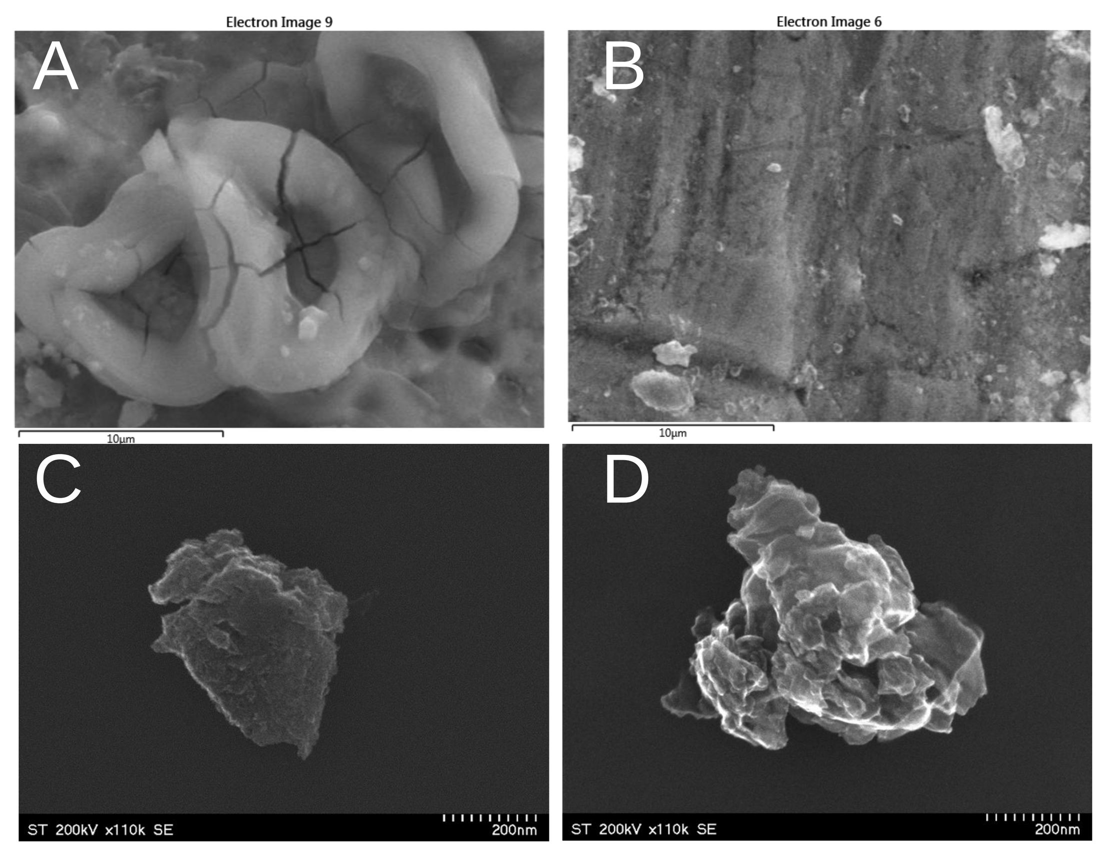

Fig. 2. *SEM micrographs (A,B) and TEM images (C,D) realized after corrosion tests in the corrosive solution: in the absence (A,C) and in the presence of Citronella oil (B,D)*

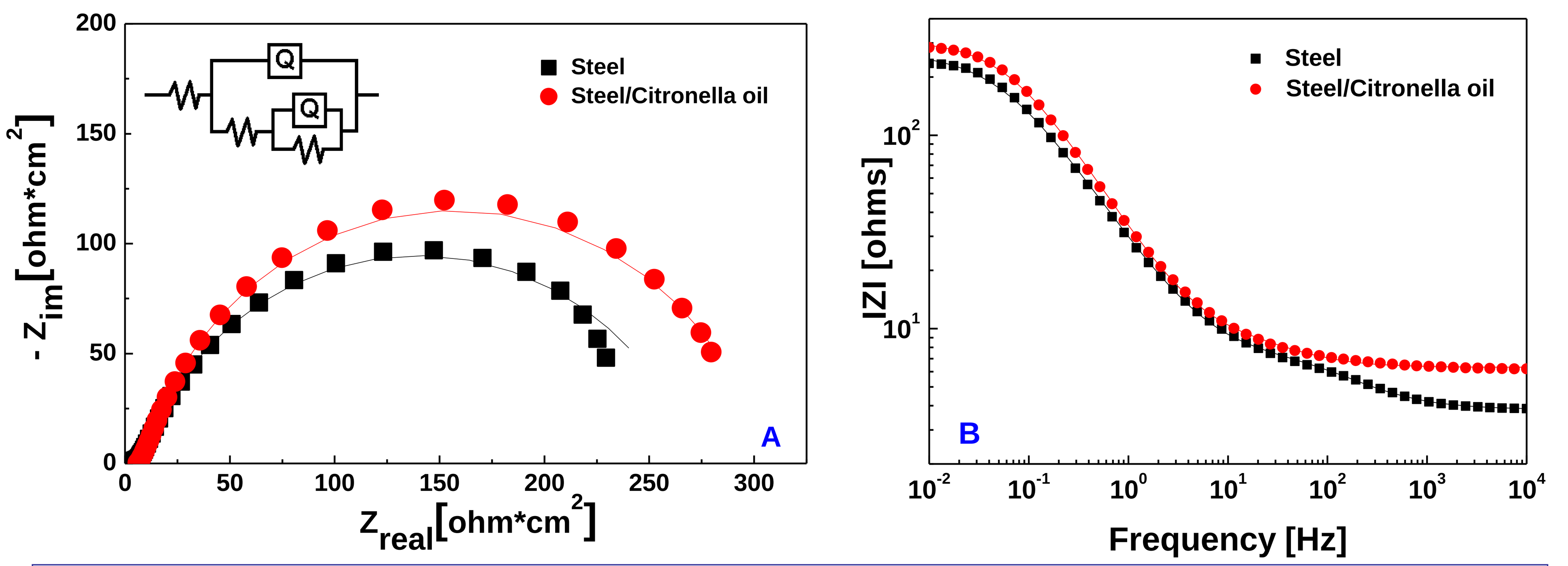

Fig. 3. *Nyquist (A) and Bode (B) plots of carbon steel electrodes in 3.5 wt.% NaCl solution in absence and presence of Citronella oil, the lines represent fitted data. Inset A is 2RQ electrical circuit*

Table 2. *Kinetic parameters of carbon steel corrosion in corrosive solution with and without green inhibitor.*

Green inhibitor	R_e [Ω*cm^2]	R_{ct} [Ω*cm^2]	*C_{dl} [mF/cm^2]	n_{dl}	R_F [Ω*cm^2]	*C_F [mF/cm^2]	n_F
-	3.81	4.40	0.34	0.76	264.70	8.28	0.79
Citronella oil	6.34	8.20	1.62	0.82	291.20	3.48	0.85

$*C = (R^{1-n}Q)^{1/n}$

AFM measurements were performed using a Cypher S AFM (Asylum Research, Oxford Instruments). AFM images were obtained in amplitude modulated AC mode (aka tapping mode) using AC160TSA-R3 (Olympus) silicon probes (f = 300 kHz, k = 26 N/m), in ambient conditions. Surface roughness is a key factor for corrosion resistance in stainless steel. The uniformity and roughness of samples surface were investigated by AFM, presented below in Fig. 4. Modified electrode shows a considerable decrease in roughness and area percent (area percent: 12% for steel/C. oil *vs.* 82% for unmodified sample).

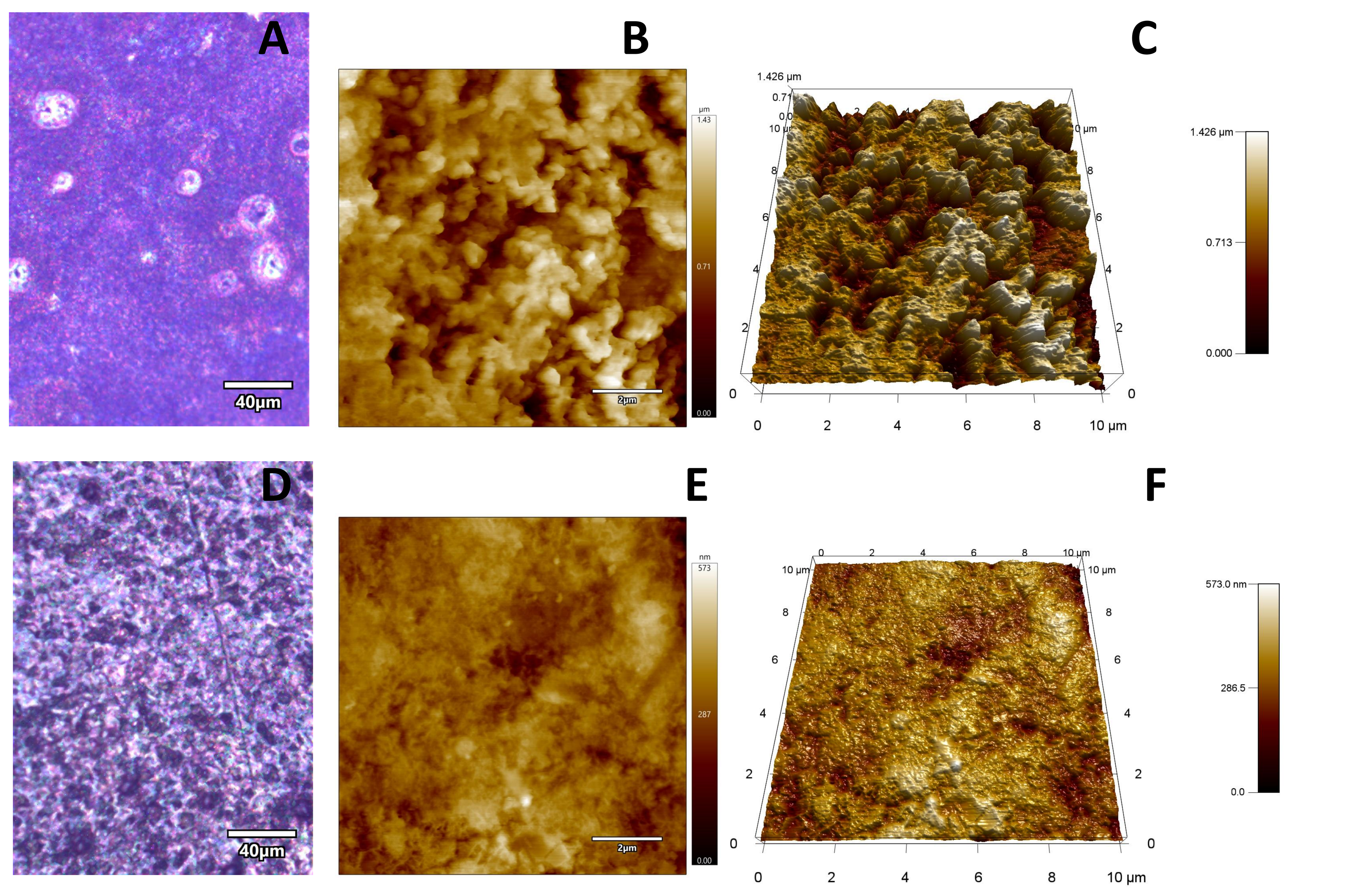

Fig. 4. *Optical and AFM images of samples corroded in NaCl 3.5 wt.% as follows: steel (A,B,C) and steel/Citronella oil (D,E,F). Figure. (From left to right): Optic images of surface, 2D/3D (10 x 10 μm^2) AFM images, white bar 2 μm, Z color range: 0÷Zmax. Top: untreated steel, bottom: steel covered with thin layer of oil before*

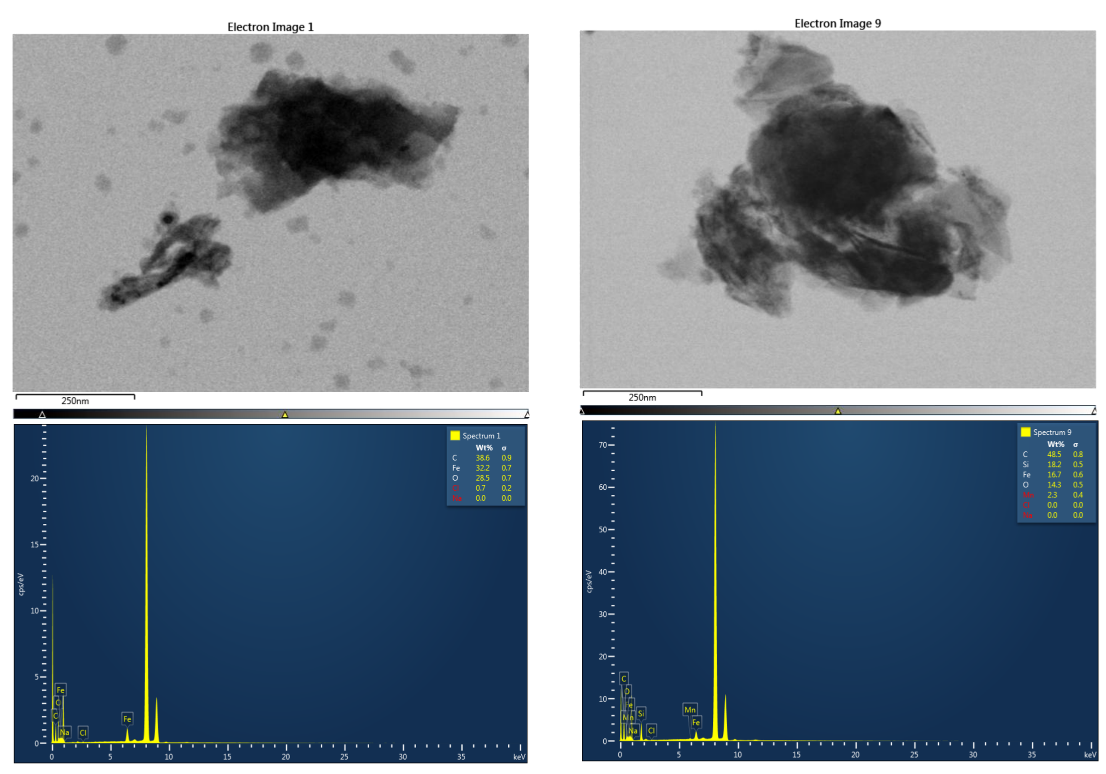

Fig. 5. *SEM-EDS* analysis after corrosion tests in the corrosive solution: in the absence (left) and in the presence of *Citronella oil* (right)

Conclusions

•Electrochemical investigations (polarization and impedance measurements) revealed that the green inhibitor used in this study exerts a good protective effect against steel corrosion in simulated seawater solution (PE = 80,4 %).

•The corrosion behavior of the steel immersed in corrosive solution 3.5 wt.% NaCl can be simulated with a 2RC electric circuit equivalent.

•The surface uniformity and morphology investigated by TEM and SEM indicate a surface protected by the C. oil. Also, this is evidenced by AFM analysis where it shows a decrease in surface roughness. The results are in concordance with electrochemical investigations.

Acknowledgements

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