GREEN CORROSION INHIBITIONS FOR 1045 AND 1080 CARBON STEELS BY GARLIC IN DYNAMIC CONDITIONS FOR IN SULPHURIC ACID MEDIA.

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Abstract

Previous studies showed the adequate efficiency of green corrosion inhibition of 1018 carbon steel in 0.5 M H_2SO_4 by garlic extract (*Allium sativum*) in static conditions at 25 °C. In this condition, the inhibition efficiency was 95 % at 400 ppm. Another study under similar conditions, showed an inhibition efficiency of 80% for 1045 steel (with 800 ppm inhibitor) and 70% for 1080 steel (with 400 ppm inhibitor). Here, the effect of dynamic conditions in the corrosion inhibition by garlic extract for these steels exposed in 0.5 M H_2SO_4 at 25 °C was investigated. In order to investigate the effect of dynamic conditions, a rotating cylinder electrode was used at 0, 250, 500, 1000 and 2000 rpm. The inhibitor efficiency was obtained by potentiodynamic polarization measurements and spectroscopy electrochemical impedance. The results indicated that the green inhibitor efficiency behaves somewhat different for both carbon steels in particular at 2000 rpm. In this condition, the inhibition efficiency was 77% for the 1080 carbon steel and 95 % for the 1045 carbon steel. According to the electrochemical tests in the present work, it seems that the garlic extract acts for both steels as a mixed type green inhibitor. This research shows that the garlic extract is a good candidate as a green inhibitor to be used in new possible environmental friendly corrosion inhibitor formulations.

Keywords: *Allium sativum*, carbon steel, garlic, green corrosion inhibitor, dynamic corrosion.

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1. INTRODUCTION

Corrosion is a general due to the alteration and destruction the most of metallic materials made for men. In recent years many searches are development to this type of damage for gives control alternatives and reduction of solutions (Ramírez-Reyes, 2005).

Actually one of the most versatile methods is the use of inhibitors to reduce corrosion velocity. The corrosion reduces the time services of metallic components, these aspects is the most importance for control (Guang-Ling, 2014). The inhibitors are substances used at low concentration to control the corrosion effects in industrial process thought come in contact of aqueous solutions ().

The inhibiting action of inhibitors is attributed to their adsorption to the metal/solution interface. It has been observed that adsorption depends mainly on certain physico-chemical properties of the inhibitor group. Like functional groups, aromaticity, electron density at the donor atoms and π-orbital character of donating electrons and also the presence of hetero-atom such as N, O and S, as well as multiple bonds in their molecular structure, are assumed to be active centers of adsorption (Rodríguez-Valdez et al, 2005).

On the other hand, there are several reports showing that the inhibition efficiency of heteroatom containing compounds increase in the order $O < N < S < P$ (Hmamou et al 2012a; Ghazoui, et al 2013; Guendouz, 2013). But the toxic of most corrosion inhibitors made us heading for the use of environment-friendly inhibitors (Barouni, 2008).

This is the one of most important reason for search to green corrosion inhibitors, because they are friendly to the environmental and safe to man. Some studies made to the natural compound as corrosion inhibitors have proven this fact. In this way, organic and aqueous natural extracts of different plants are tested. *Chenopodium ambrosioides* (Rodríguez-Clemente et al 2011); *Rosmarinus officinalis* (Velázquez-González et al, 2014); *Prosopis laeavigata* (Ramírez-Arteaga et al, 2013); *Eucalyptus globulus* (Rekkab et al, 2012), Chamomile (Hmamou et al, 2012b). As well some fruits and species such as *Grape pomace* (da Rocha et al, 2012), *Thymus vulgarise* (Fouda et al, 2014); Avocado (Belkhaouda et al, 2013) and *Capsicum annum* (Ji et al, 2012) are studied as green corrosion inhibitors.

The natural and green corrosion inhibitors tested have been reported to be excellent inhibitors for metals and alloys in acid solutions. The inhibition efficiency effect of the natural extract can be attributed to adsorption of organic substances on the metals and alloys surface consequently blocking active sites or even forming a protective barrier (Amitha and Basu, 2012). This would be especially important if additives used from green extracts to be do oxidative stabilization (antioxidants) or corrosion protection as green corrosion inhibitors (Sulaiman et al, 2012).

Many vegetal species know as antioxidants such as “garlic” (Allium sativum). For it reported at least 33 sulphur compounds which are responsible for pungent odour garlic and some important biological effects (Rahman and Lowe, 2006). The garlic bulb contains approximately 1% of alliin, moreover if the garlic is crushed or cut activates the enzyme allinase, which metabolizes alliin to allicin (Lawson, 1998).

In order to contributing with the green corrosion inhibitors in the present work, the behavior of hexane extract of Allium sativum was evaluated at different concentrations as green corrosion inhibitor on carbon steel in 0.5 M sulfuric acid thought using some electrochemical techniques as potentiodynamic polarization and electrochemical impedance spectroscopy measurements.

2. EXPERIMENTAL METHODOLOGY

2.1. Green organic inhibitor

The Allium sativum, commonly known as garlic, was purchased commercially. The garlic bulbs were cleaned and cut in small pieces and put it in Erlenmeyer flask and extracted by maceration used hexane and left 24 h at room temperature. The solvent was eliminated by rotary evaporator. The solvent recovered was place back into the glass container with the garlic again this process was repeated twice times. The organic residue was considered hexane garlic extract.

2.2 Electrochemical measurements

Prior to experiment, 1045 and 1080 carbon steel was cut into coupons of dimension 7.0 cm large and 1.0 cm diameter. Employed electrochemical techniques included potentiodynamic polarization curves and impedance spectroscopy measurements, EIS.

2.3 Polarization curves and electrochemical impedance spectroscopy (EIS)

Polarization curves for 1045 and 1080 carbon steels in acidic media were recorder at two different concentrations of *A. sativum* as green corrosion inhibitor; 400 ppm for 1045 carbon steel and 800 ppm for 1080 carbon steel. At a constant sweep rate of 1 mV/s at the interval from -300 to 300 mV respect to the E_{corr} value. Measurements were obtained by using a conventional three electrodes glass cell with two graphite electrodes symmetrically distributed and saturated calomel electrode (SCE) as reference with a Lugging capillary bridge. EIS measurements were done at E_{corr} by applying a sinusoidal signal with amplitude of 10 mV in the frequency range of 0.05-20000 Hz. Corrosion current density values, I_{corr}, were obtained by using Tafel extrapolation by taking an extrapolation interval of 250 mV around the E_{corr} value. Inhibitor efficiency was calculated according the equation 1.

$$IE(\%) = \frac{(I_{corr,b} - I_{corr,i})}{I_{corr,b}} X100 \quad \textbf{(1)}$$

were i_{corr}, and I_{corrb} are the corrosion current density values with and without inhibitors respectively.

A Zanher zenium potentiostat controlled by a desk top computer was used for the polarization curves, whereas for the EIS measurements. Electrochemical impedance spectroscopy (EIS) test carried out at Ecorr by using signal amplitude of 10 mV in a frequency interval of 100 mHz - 100 KHz. A VerSAT potentiostat controlled by a desk top computer was used for the polarization curves.

Then data EIS can be calculated, the charge transfer resistance (Rct) and capacitance of the double electrochemical layer (Cdl) and the Rf represents the resistance of the corrosion products film and Cf its capacitance. However, the double-layer capacitance Cdl can also be calculated from the equation 2.

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad \textbf{(2)}$$

Were the frequency value at which the imaginary component of the impedance is maximal.

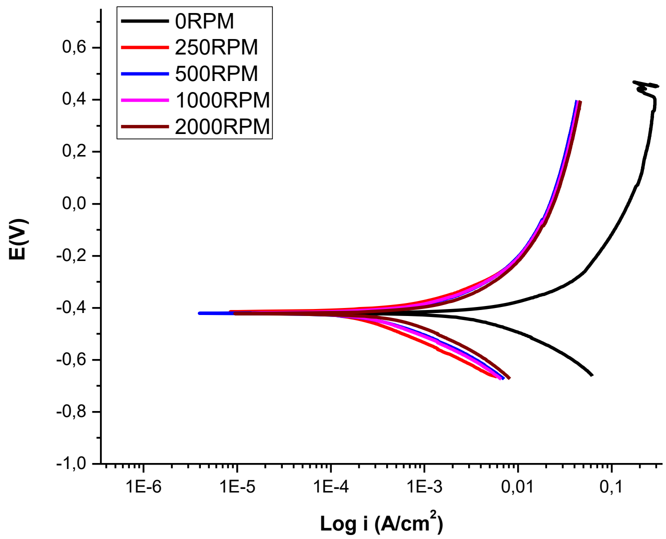
3. RESULTS AND DISCUSSION

3.1 Electrochemical curves in dynamic conditions for corrosion inhibition employed *A. sativum* at 25 °C.

The resistance to corrosion characterization were carried out polarization curves and EIS for 1045 and 1080 carbon steels in acid medium at 25 °C and at different rotations velocities as 0 to 2000 rpm. *A. sativum* was employed the optimal concentration of green corrosion inhibitor at 400 ppm to 1045 carbon steel and 800 ppm 1080 carbon steel. The rotatory dish is a dynamic test that allows to determining the mass transfer on the surface electrode, the solution flow makes a resisting to formation of the diffusion layer and the thickness depending on the speed.

3.2 Corrosion inhibition of 1040 carbon steel in acid media using 400 ppm of *A. sativum* as green inhibitor in dynamics conditions at 25 °C

The polarization curves shown in the graphic 1, it is possible see the corrosion potential values (E_{corr}) move to less negative values (-0.427 to -0.418 V), with the increased of rotational speed. Indicating that corrosion slows, the corrosion density do not affect with the rotational speed. However, the anodic current increase a little bet when the cathode current decreases (Lahhit *et al* 2011).



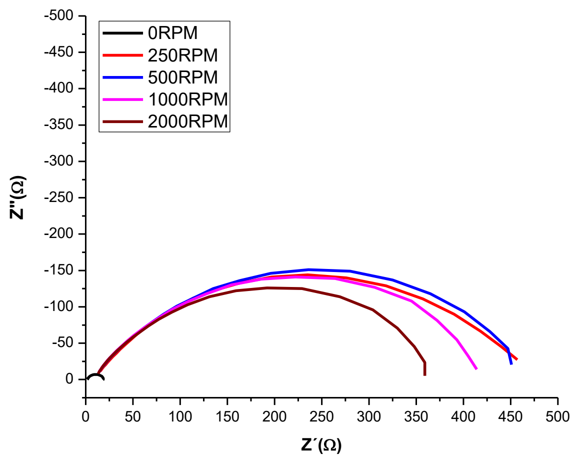
Graphic 1. Polarization curves for 1045 carbon steel in 0.5 M H_2SO_4 employing 400 ppm of *A. sativum* at 25 °C in dynamic conditions

From the graphic 1 were extracted some dates and some other were calculated there were corrosion current (I_{corr}), corrosion potential (E_{corr}), Tafel slopes for the anodic and cathode branches (βa, βc) and the corrosion velocity (V_{corr}). All dates is displaying on the table 1. The best corrosion inhibition efficiency (IE %) was obtained at 2000 rpm.

Table 1. Electrochemical parameters from polarization curves of 1045 carbon steel at 25 °C using 400 ppm of *A. sativum* as green corrosion inhibitor in dynamic conditions

Rotational speed (rpm)	E_{corr} (mVECS)	I_{corr} (mA/cm^2)	βa (mV/dec)	βc (mV/dec)	IE (%)
0	-0.414	0.068	305	590	--
250	-0.427	0.986	390	625	93.1
500	-0.414	0.214	418	405	68.2
1000	-0.418	0.214	418	405	68.2
2000	-0.418	0.947	558	540	72.4

The Nyquist diagrams were obtain with the same experiments and showing in the graphic 2. Is possible see a capacitive depressed semicircle, with shaft in the real center. The semicircle diameter decreased to increase the rotational speed; it was suggest the velocity corrosion increased. Could be the oxygen mass transport increased on the metal surface by the rotation and producing a general oxidation (Pascale Bommersbach et al 2005, W. Stephen Tait 1994).



Graphic 2. Nyquist diagram for 1045 carbon steel employed 400 ppm of A. *sativum* as green corrosion inhibitor at 25°C in dynamic conditions.

From the graphic 2 were obtained some dates and others were calculated as the resistance of charger transfer (R_{ct}), maximum frequency (F_{max}), and the double layer capacitance (C_{dl}), everything dates shown on table 2. Could observe the increased of rotational speed to denoted the efficiency of the inhibitor. (Bouckamp, 1993; Mac Donald, 1997).

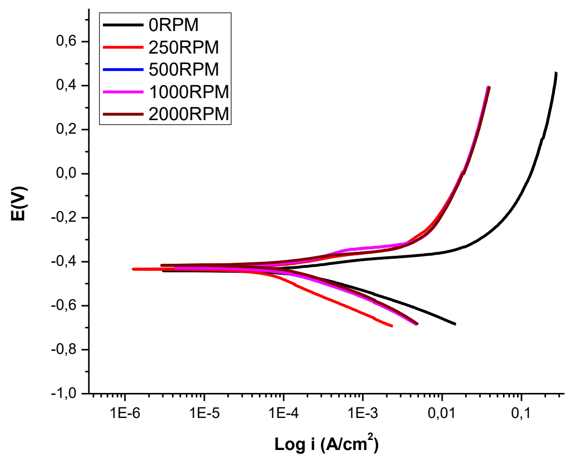
Table 2. Electrochemical parameters from EIS of 1045 carbon steel at 25 °C using 400 ppm of *A. sativum* as green corrosion inhibitor in dynamic conditions

Rotational speed (rpm)	R_{ct}(Ω cm^{-2})	F_{max} (Hz)	C_{dl} (μF.cm^{2})
0	18.20	70.8	1.23E-4
250	456.59	13.5	2.58E-5
500	450.45	9.44	3.74E-5
1000	411.81	13.5	2.86E-5
2000	358.63	13.5	3.28E-5

3.3 Corrosion inhibition of 1080 carbon steel in acid media using 800 ppm of *A. sativum* as green inhibitor in dynamics conditions at 25 °C

In the polarization curves shown on graphic 3, the current density moves to anodic portion when the potential tends to take positive values. Because a desorption processes occurs of the layer formed for the corrosion products. However, when the potential is less it seems that the inhibitor reached to stable state, observe the cathodic branch, it was controlled by mass transport. It is possible see to change the low values current density when the rotational spped of electrode increased, this change correspond by hydrogen evolution, because the flow velocity don't made effect.

Is possible appreciate that the inhibitor affect the potential of corrosion in all cases, because it moves to noble potentials and it could probability formed a protecting layer on material surface and protects the metal of aggressive environment, it effect describes an anodic inhibitor, that the anodic reaction was modified.



Graphic 3. Polarization curves for 1080 carbon steel in 0.5 M H_2SO_4 employing 800 ppm of *A. sativum* at 25 °C in dynamic conditions

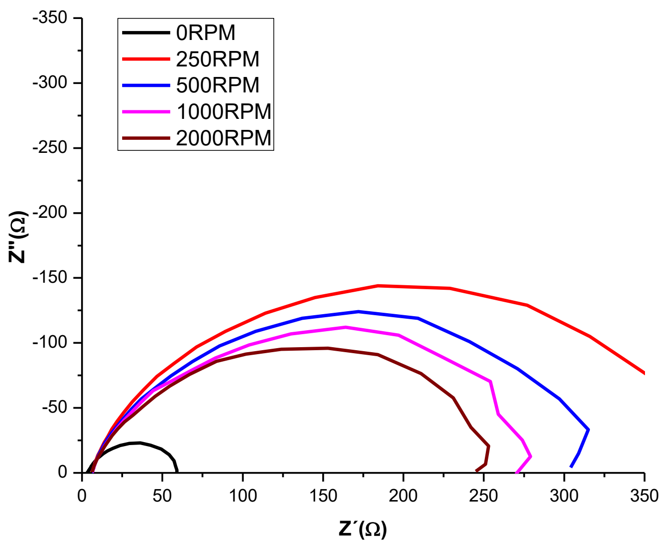
The electrochemical parameters obtained to polarization curves were processes and build the table 3. Is possible to seen that the 250 rpm produced the best inhibition efficiency percentage for the good corrosion current.

Table 3. Electrochemical parameters from polarization curves of 1080 carbon steel at 25 °C using 800 ppm of *A. sativum* as green corrosion inhibitor in dynamic conditions

Rotational speed (rpm)	E_{corr} (mVECS)	I_{corr} (mA/cm^2)	βa (mV/dec)	βc (mV/dec)	IE (%)
0	-0.441	0.157	364	676	--
250	-0.427	0.490	214	234	67.9
500	-0.418	0.400	350	342	60.7

1000	-0.427	0.410	323	331	61.7
2000	-0.396	0.413	342	331	61.9

The EIS dates show on the graphic 4. Depressed and flatter semicircles are observed in all rotation velocities employed. Diameter of semicircles decreases gradually according to increasing rotational speed (500, 1000 and 2000 rpm), only at 250 rpm shown the biggest semicircle (Rct = 350 $\Omega\ cm^{-2}$) indicates the major opposition to charge by mass transportation control.



Graphic 4. Nyquist diagram for 1080 carbon steel employed 800 ppm of A. *sativum* as green corrosion inhibitor at 25°C in dynamic conditions.

The organized and classified date's derivatives of Nyquist diagram are showing on table 4.

Table 4. Electrochemical parameters from EIS of 1080 carbon steel at 25 °C using 800 ppm of *A. sativum* as green corrosion inhibitor in dynamic conditions

Rotational speed (rpm)	R_{ct} (Ω cm^{-2})	F_{max} (Hz)	C_{dl} ($\mu F.cm^2$)
0	59.18	13.5	1.99E-4
250	299.72	18.7	2.83E-5
500	300.95	13.5	3.91E-5
1000	258.95	13.5	4.55E-5
2000	253.36	13.5	4.65E-5

Total results of all experiments obtained by EIS could be observed better on the table 5. Observing that the dynamic conditions that give the best corrosion efficiency inhibition, in both metals was at 250 rpm. Nothing that the *A. sativum* produced 95.4% corrosion efficiency inhibition to 1045 carbon steel and 82.3% corrosion efficiency inhibition to 1080 carbon steel.

Table 5. EIS results from *A. sativum* as green corrosion inhibitor in dynamic conditions for both metals

1045 carbon steel with 400 ppm of green inhibitor		**1080 carbon steel with 800 ppm of green inhibitor**	
V(rpm)	EI (%)	V(rpm)	EI (%)
250	**95.4**	**250**	**82.31**
500	95.4	500	79.74
1000	94.1	1000	79.74
2000	95	2000	77.35

CONCLUSIONS

In dynamic conditions was possible inhibit the corrosion of 1040 and 1080 carbon steels in acid media thought employed *A. sativum* as green corrosion inhibitor at room temperature. The bets corrosion efficiency inhibition was obtained by EIS at 250 rpm for both metals, there were 82.3% for 1040 carbon steel and 82.3% for 1080 carbon steel.

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