

Hexane Extract of *Allium sativum* as a Corrosion Inhibitor for Carbon Steel in 0.5 M H₂SO₄

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Abstract

The corrosion inhibition of 1018 carbon steel in 0.5 M H₂SO₄ was conducted by using an organic extract of natural origin. The evaluation corrosion inhibition activity of hexane extract of *Allium sativum* was carried out by electrochemical tests such as polarization curves and electrochemical impedance spectroscopy. Different temperatures were employed room temperature, 40° and 60° C. The inhibitor concentrations were 0, 50, 100, 200, 400, 600 and 800 ppm. The organic extract acts as corrosion inhibitor mixed and efficiency of corrosion inhibition increases linearly concentration, the major efficiency of corrosion inhibition was up 90 percent used 400 ppm of *A. sativum* extract at room temperature. The efficiency corrosion inhibition is affected by temperature increased.

Keywords: *Allium sativum*, natural inhibitor, acid corrosion, electrochemical techniques.

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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).

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Actually one of the most versatile methods is the use of inhibitors to reduce corrosion velocity. The corrosion limit the services time of metallic components, these aspects is the most importance to 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 these 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 2012; Ghazoui, et al 2013; Guendouz, 2013). But th 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 corrosion inhibitors 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 extracts of different plants are tested, *Chenopodium ambrosioides* (Rodríguez-Clemente et al 2011), *Rosmarinus officinalis* (Velázquez-González et al, 2014), *Prosopis leavigata* (Ramírez-Arteaga et al, 2013), *Eucalyptus globulus* (Rekkab et al, 2012), Chamomile (Hmamou et al, 2012). As well some fruits and species as *Grape pomace* (da Rocha et al, 2012), *Thymus* (Fouda et al, 2014), *Avocado* (Belkhaouda et al, 2013), *Capsicum annum* (Ji et al, 2012) are studied as corrosion inhibitors.

The natural vegetal species tested have been reported to be excellent inhibitors for metals and alloys in acidic solutions. The inhibition efficiency effect of plant 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 vegetable extracts to be do oxidative stabilization (antioxidants) or corrosion protection (corrosion inhibitors) (Sulaiman et al, 2012).

Many vegetal species know as antioxidants as “garlic” (*Allium sativum*) because contain contains at least 33 sulphur compounds which are responsible for both garlic’s pungent odour and many 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 various concentrations as inhibitor of corrosion on carbon steel in 0.5 M sulfuric acid solution by using potentiodynamic polarization measurements, electrochemical impedance spectroscopy and weight loss method.

2. EXPERIMENTAL METHODOLOGY

2.1. Organic extract

The plant, known as *Allium sativum*, was purchased commercially. The garlic bulbs were cleaned and cut in small pieces and put in Erlenmeyer flask and extracted 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. The resulting extract was analyzed by FTIR. The hexane garlic extract tested for their activity as inhibitors of corrosion by dilution the concentrations used were 50, 100, 200, 400, 600 and 800 ppm.

2.2. Electrochemical measurements

Prior to experiment, mild 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.

2.2.1. Polarization curves.

Polarization curves for 1018 carbon steel in different concentrations of the inhibitor *A. sativum* in acidic media were recorder at a constant sweep rate of 1 mV/s at the interval from -1500 to 1500 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.

The specimen was polarized around about ± 300 mV respect the free corrosion potential, E_{corr} . The scanning speed was 1 m V / sec, continuously recording the current with the change in potential. 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.

$$IE(\%) = \frac{(I_{corr,b} - I_{corr,i})}{I_{corr,b}} \times 100 \quad (1)$$

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

2.2.2. Electrochemical impedance spectroscopy (EIS)

The EIS test carried out at E_{corr} by using signal amplitude of 10 mV in a frequency interval of 100 mHz-100 KHz. An ACM potentiostat controlled by a desk top computer was used for the polarization curves, whereas for the EIS measurements a model PC4

electrochemical impedance spectroscopy (EIS) test carried out at E_{corr} by using signal amplitude of 10 mV in a frequency interval of 100 mHz-100 KHz. An ACM potentiostat controlled by a desk top computer was used for the polarization curves, whereas for the EIS measurements a model PC4 300 Gamry potentiostat was used.

Then data EIS can be calculated by using equivalent circuits as that show in figure 00. The charge transfer resistance (R_{ct}) and capacitance of the double electrochemical layer (C_{dl}) and the R_f represents the resistance of the corrosion products film and C_f its capacitance. However, the double-layer capacitance C_{dl} can also be calculated from the equation 2.

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

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

2.3. Corrosion efficiency inhibition gravimetric weight loss experiment

Mild steel sheet was cut into coupons of dimensions was 3 cm large and 1.0 cm diameter. These were abraded gradually with 240 to 600 grades of emery paper, degreased in absolute ethanol, dried and stored in acetone before of used.

During the experiments, the specimens were weighed accurately and immersed in 100 ml beakers each containing 50 ml 0.5 M H_2SO_4 , with and without (blank) the addition of different concentrations of the inhibitor. The tests were carried out on triplicate to ensure reproducibility at room temperature. The aggressive acid solution was open to air, and after 72 hours the specimens were taken out, washed with distilled water, dried and weighed accurately. Specimens were weighed in an analytical balance with a precision of 0.1 mg. Corrosion rates were calculated as equation 3.

$$\Delta W = \frac{(m_1 - m_2)}{A} \quad (3)$$

Were m_1 is the mass of the specimen before corrosion, m_2 is the mass of the specimen after corrosion and A is the exposed area of the specimen. The inhibition efficiency of the weight loss weight (IEW) was calculated as equation 4.

$$IEW(\%) = \frac{(\Delta W_1 - \Delta W_2)}{\Delta W_1} \times 100 \quad (4)$$

Were W_1 is the weight loss without inhibitor and W_2 is the weight loss with inhibitor.

3. RESULTS AND DISCUSSION

3.1. Analysis FTIR hexane extract *A. sativum*

The yield of hexane extract of *A. sativum* recovered after extraction and free of solvent was 2 percent. The Analysis of FTIR of extract show in figure 1. It can see the finger print of sulfur compounds

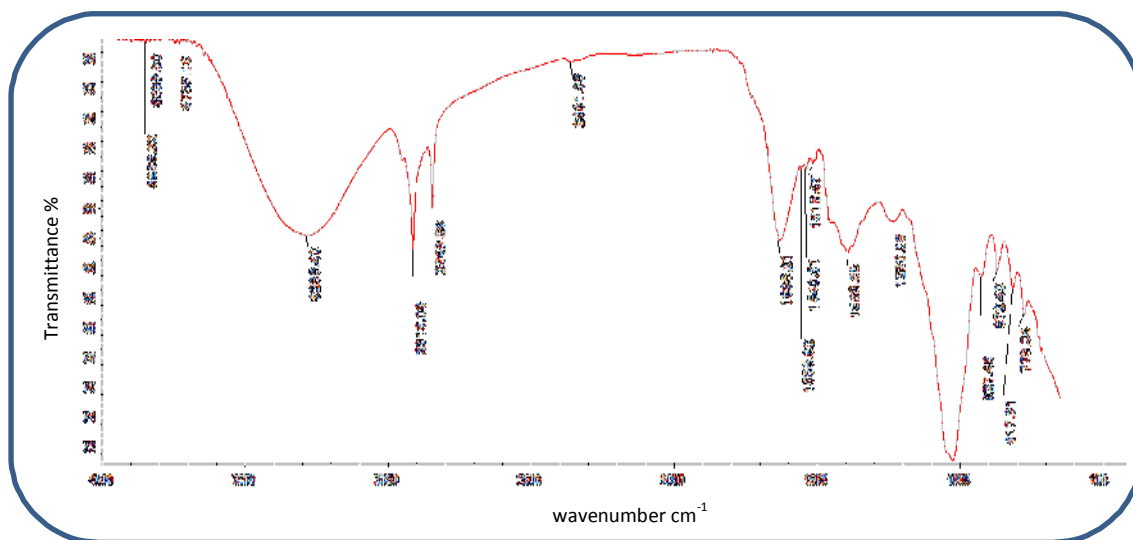


Figure 1. Infrared spectroscopy of pure hexane extract of *Allium sativum*.

Figure 1 shows the FTIR spectrum for pure *Allium sativum* extract where it can be seen that broad bands in the range of 3000-3600 cm^{-1} can be assigned to the OH stretching vibrations of the crude hexane extract. The spectrum provides the “fingerprint” region which reflects information about sulphur compounds as components in the crude extract of garlic, with a signal at 778 cm^{-1} assigned to C-S bond; a strong signal at 1016 cm^{-1} from thionyl group (S=O) and the vinyl group appeared at 1236 cm^{-1} and at 927 cm^{-1} due to the C=C-H group (Stuart, 2004). These aspects are concordant with the chemistry reports for *A. sativum*, it has many sulphur compounds.

The IR information of hexane extract garlic, suggests the presence of allicin in the crude hexane extract (figure 2a). The rest of the signals are at 3244 cm^{-1} , a stronger

signal which corresponds to hydroxyl group (-OH), at 1732 cm^{-1} a strong signal correspond to carboxylic bond (C=O) and 1219 cm^{-1} due to acyl, C-O, group. At 2848 and 2920 cm^{-1} appeared the stretching signal from the CH_2 - group, symmetric and asymmetric respectively. This information could be assigned for the fatty acids (figure 2b) and suggest the presence of them in the hexane extract of garlic (Rahman and Lowe, 2006). In the fatty acids structure, $-\text{CH}_2$ - groups are present and the scissoring signal from these groups appeared in IR spectrum at 1462 cm^{-1} .

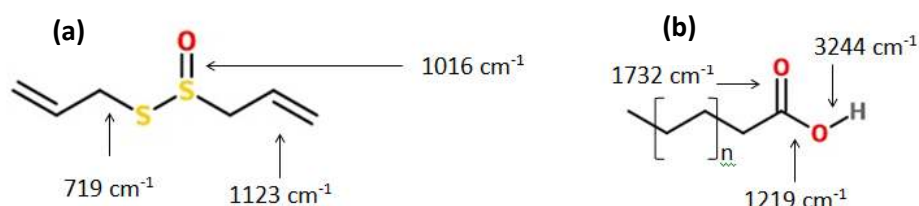


Figure 2. Structures and fragments of natural compounds presents in hexane extract of *A. sativum* and wave number from representative groups.
(a) alliin, (b) General structure of fatty acid.

3.2. Polarization curves

The polarization curves for 1018 carbon steel in different concentrations of the inhibitor *A. sativum* in acidic media at room temperature show in figure 3. The corrosion current values (i_{corr}), the corrosion potential (E_{corr}), Tafel slopes of cathodic and anodic (β_{C} and β_{A}) and inhibition efficiency (% E) showed in the tables with the electrochemical parameters and have been calculated.

Inspection of curves in figure 3 reveals that the addition of hexane extract of *A. sativum*, has a slight effect in both polarization curves, this indicates that inhibitor acts as mixed type inhibitor. The highest efficiency inhibition for 1018 carbon steel in acid media at room temperature was obtained used 400 ppm of hexane extract of *A. sativum* in this concentration the i_{cor} 39.8 mA/cm² if was the lowest valium and the efficiency inhibition was 96 percent.

- 1 0 0
- 2 0 0

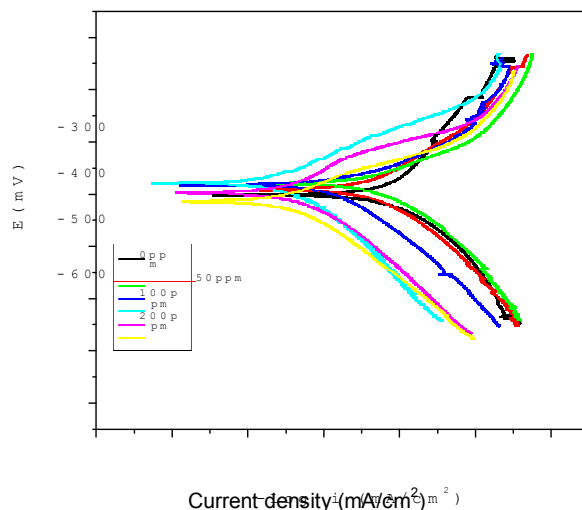


Figure 3. Polarization curves for 1018 carbon steel in 0.5M H₂SO₄ in different concentrations of *Allium sativum* at 25°C

Table 1. Electrochemical parameters obtained from polarization curves at 25 °C

C_{inh} (ppm)	E_{corr} (mVECS)	i_{corr} (mA/cm²)	β_a (mV/dec)	β_c (mV/dec)	EI (%)
0	-435	630.9	234	213	--
50	-424	794.3	190	229	-25.8
100	-415	1258.9	164	264	-99.5
200	-415	199.5	93	207	68.3
400	-408	25.1	157	291	96
600	-433	39.8	248	240	93.6
800	-450	50.11	150	300	92.05

3.3. Electrochemical Impedance Spectroscopy curves

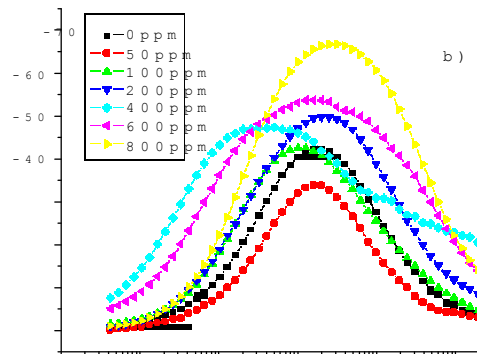
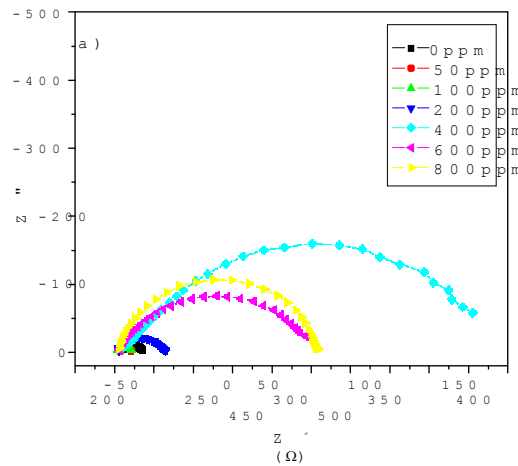
The effect of *A. sativum* concentration on Nyquist and Bode diagrams for carbon steel in 0.5 M H₂SO₄ at 25 °C is shown in figure 4. Nyquist diagrams show that data display a single capacitive like, depressed semicircle with their centers below the real axis at all frequency values.

The graphics show in figure 4 indicate that the corrosion process is under charge transfer control from the steel to the electrolyte through the double electrochemical layer. The polarization resistance increased with increasing inhibitor concentration.

The polarization resistance R_p increases largely from 32.9 to 458.52 Ω and the electric double layer capacitor C_{dl} decreased from 1.53 X 10⁻⁴ to 3.47 X 10⁻⁵ μF•cm⁻² with

increase the hexane extract of *A. sativum* from 0 to 400 ppm. It shows decrease of active surface of carbon steel by the adsorption of the inhibitor, in this way the corrosion process was prevented. Without inhibitor, carbon steel exhibited a low polarization resistance due to the easy attack of the corrosive acid medium on carbon steel surfaces.

In other hand the Bode diagrams figure 4b shows only one peak around 100 Hz for the uninhibited solution, which indicates the absence of any protective layer in that case. However, when *A. sativum* is added to the solution, the phase angle starts to increase with the frequency and it remains constant in a relatively wide range of frequency, especially with the addition of 400 ppm of inhibitor, in both two graphics Bode impedance and Bode phase angle plot (figures 4b and 4c). The fact that the angle phase remains constant in a wide frequency interval indicates the formation of a protective layer formed by the inhibitor and Fe^{2+} ions on steel surface, forming metal-inhibitor complexes. This frequency interval where the angle phase remains constant decreases for inhibitor concentrations higher than 400 ppm, indicating that the formed protective layer loses its protectiveness, bringing an increase in the corrosion rate.



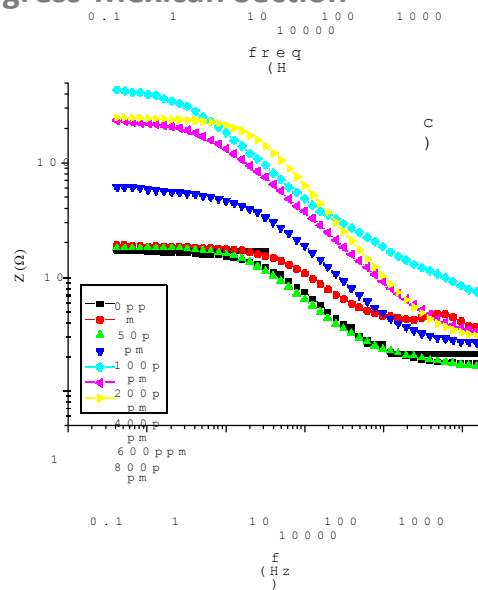


Figure 4. Spectroscopy Impedance Electrochemistry the effect of 1018 carbon steel at room temperature use hexane extract of *A. sativum* as inhibitor. a) Nyquist diagram, b) and c) Bode diagrams

Table 2. Electrochemical parameters obtained from Nyquist curves at 25 °C use hexane extract of *A. sativum* as inhibitor.

C_{inh} (ppm)	R_{ct} (Ohm cm^2)	F_{max} (Hz)	C_{dl} ($\mu F.cm^2$)	FI (%)
0	32.9	31.57	1.53×10^{-4}	---
50	17.98	15.79	5.60×10^{-4}	-82.98
100	17.98	15.79	5.60×10^{-4}	-82.98
200	64.2	12.50	1.98×10^{-4}	48.75
400	458.42	9.99	3.47×10^{-5}	92.82
600	237.59	9.99	6.70×10^{-5}	86.15
800	259.6	6.31	9.71×10^{-5}	87.32

3.4. Corrosion efficiency inhibition gravimetric weight Loss

The effect of inhibitor concentration on the corrosion efficiency inhibition for the test weight loss for 1018 carbon steel in 0.5 M H_2SO_4 at room temperature shows in table 3. The corrosion rates values decrease when the concentration of hexane extract of *A. sativum* increases. From the analysis of table 3 it is very clear that protection efficiency increased with the increase in concentration from 50 to 400 ppm for the green inhibitor studied. Which suggested that the corrosion inhibition might be caused by the inhibitor adsorption onto the steel surface starts to increase (25).

Table 3. Corrosion efficiency inhibition of 1018 carbon steel at room temperature for hexane extract of *A. sativum* as inhibitor for gravimetric weight loss.

C_{inh} (ppm)	ΔW%	WE%
0	26.9	----
50	32.5	17.23
100	31.9	38.86
200	38.9	38.86
400	19.0	91.57
600	24.7	-8.90
800	31.1	-7.64

3.5. Studies corrosion inhibition at 40 and 60 °C

The concentration hexane extract of *A. sativum* gives the best efficiency inhibition for corrosion 1018 carbon steel in acid media at room temperature was evaluated at 40 and 60°C. The results show the efficiency inhibition decrease with the temperature increasing. The efficiency inhibition decrease from 90 (at room temperature) to 45 percent at 40 and 60 °C. Is clear to see that the chemical nature of inhibitor modified with the temperature increasing and its activity loss.

4. CONCLUSIONS

This study showed the excellent corrosion inhibitor for carbon steel in 0.5 M H₂SO₄ at room temperature for hexane extract of *A. sativum*. The best action is attained in the presence of 400 ppm (0.4 g/L) of hexane extract of *A. sativum*. The promotion of formation of a chelate on the metal surface, which includes the transfer of electrons from the organic compounds, present in the hexane extract of *A. sativum* as allicin, to metal forming coordinate covalent bond during such chemical adsorption process. This hypothesis could be corroborated with the metallographic analysis. The hexane extract of *A. sativum* could be considerate as excellent green corrosion inhibitor for mild steel in acid medium.

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