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Allium sativum as Corrosion Inhibitor for Carbon Steel in Sulfuric Acid

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A study on the use of *Allium sativum* (garlic) as corrosion inhibitor for carbon steel in 0.5M H_2SO_4 has been carried out by using potentiodynamic polarization curves, electrochemical impedance spectroscopy and weight loss measurements. Inhibitor concentrations included 0, 100, 200, 400, 600 and 800 ppm at 25, 40 and 60^0C. *Allium sativum* has been proved to be good inhibitor, reaching its highest efficiency, 96%, with the addition of 400 ppm. This reduction in the corrosion rate was due to the formation of an external layer formed by S-containing film present in the extract which was adsorbed physically on the steel surface. *Allium sativum* acted as a mixed type of inhibitor.

Keywords: Carbon steel, green inhibitor, acidic corrosion.

1. INTRODUCTION

Metals corrosion causes big losses to the industry and one of the most widely used methods to fight it is the use of corrosion inhibitors. The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations have compelled and motivated researchers to focus on the need to develop cheap, non-toxic and environmentally benign natural products such as leaves, fruits or seeds extracts, which can be used as corrosion inhibitors. It can be found in the literature a big amount of research works related with the use of natural products extracts to be used as "green" corrosion inhibitors due to the presence of complex organic species such as tannins, alkaloids, carbohydrates and proteins as well as their acid hydrolysis products [1-20]. The use of these natural products are more effective and highly environmentally benign compared to organic and inorganic

inhibitors used in chemical or any industrial applications. Some of the natural products which have been proved to be good corrosion inhibitors are Aloe [2], *Coriandrum sativum* [3], *Green Bambusa Arundinacea* leaves [4], *Artemisia pallens* [5] and Phyllanthus fraternus [7] among others.

The use of garlic as a medicine and condiment predates written history. The oldest recorded literature from the Sumerians is dated at 2600–2100 B.C. Botanically, *Allium sativum* is a member of the *Lillaceae* family, along with onions, chives and shallots. Garlic is one of the edible plants which has generated a lot of interest throughout human history as a medicinal panacea. A wide range of microorganisms including bacteria, fungi, protozoa and viruses have been shown to be sensitive to crushed garlic preparations. Moreover, garlic has been reported to reduce blood lipids and to have anticancer effects. Chemical analyses of garlic cloves have revealed an unusual concentration of sulfur-containing compounds (1–3%) [21, 22]. Analysis of steam distillations of crushed garlic cloves performed over a century ago showed a variety of allyl sulfides. The compound turned out to be an oxygenated sulfur compound which they termed allicin, from the Latin name of the garlic plant, *Allium sativum.*

Evidence from several investigations suggests that the biological and medical functions of garlic are mainly due to their high organo-sulphur compounds content. The primary sulphur-containing constituents in garlic are the S-alkyl-L-cysteine sulphoxides (ACSOs), such as allicin, and g-glutamylcysteines. Allicin (diallylthiosulonate), formed in nature upon crushing of garlic cloves, is responsible for the typical pungent smell as well as for the various biological activities including prominent antibiotic effects and inhibition of cancer promotion [23]. Allicin also reduces serum cholesterol and triglyceride levels as well as atherosclerotic plaque formation, prevents platelet aggregation and decreases blood pressure [24- 26]. Flavonoids, abundant in garlic, and a small amount of non-volatile water-soluble sulphur compounds found in garlic, as S-allyl cysteine (SAC), (coming from enzymatic transformation of g-glutamylcysteines when garlic is extracted with an aqueous solution), are also responsible for a great part of the health benefits of garlic. Thus, the goal of this paper, is to evaluate the inhibitory properties of *Allium sativum* for carbon steel in sulfuric acid, one of the most used reagents in the chemical industry.

2. EXPERIMENTAL PROCEDURE.

Fresh garlic (*Allium sativum* Linn) bulbs were obtained from the local market and cut into small pieces. Aproximately 1200 g of chopped garlic were soaked in 1000ml of hexane and left during 30 days until all hexane was evaporated obtaining a solid. After this, the solid was weighted and dissolved in 100 ml of hexane and used as a stock solution and used then for preparation of the desired concentrations by dilution. The aggressive solution, 0.5 M H_2SO_4 was prepared by dilution of analytical grade H_2SO_4 with double distilled water. For instance, if the solid weighted was 0.5 g and it was dissolved in 100 g of hexane, this corresponds to 500 ppm of garlic. If our cell contained 100 ml of aggressive solution, calculations had to be done to know the volume of the stock solution added to the electrolyte to have, for instance, 100 ppm of inhibitor. Corrosion tests were performed on coupons prepared from 1018 carbon steel rods containg 0.14%C, 0.90% Mn, 0.30%S, 0.030% P and as balance

Fe, encapsulated in commercial epoxic resin with an exposed area of 1.0 cm^2. Weight loss experiments were carried out with steel rods 2.5 cm length and 0.6 cm diameter abraded with fine emery paper until 1200 grade, rinsed with acetone, and exposed to the aggressive solution during 72 h. After a total time of exposition of 72 hours, specimens were taken out, washed with distilled water, degreased with acetone, dried and weighed accurately. Tests were performed by triplicate at room temperature (25 °C), 40 and 60 °C by using a hot plate. Corrosion rates, in terms of weight loss measurements, ΔW, were calculated as follows:

$$\Delta W = (m_1 - m_2) / A \quad (1)$$

were m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after corrosion, and A the exposed area of the specimen. For the weight loss tests, inhibitor efficiency, IE, was calculated as follows:

$$IE\ (\%) = 100\ (\Delta W_1 - \Delta W_2)/ \Delta W_1 \quad (2)$$

were ΔW_1 is the weight loss without inhibitor, and ΔW_2 the weight loss with inhibitor. Specimens were removed, rinsed in water and in acetone, dried in warm air and stored in a dissicator. Specimens were weighed in an analytical balance with a precision of 0.1 mg. Electrochemical techniques employed included potentiodynamic polarization curves and electrochemical impedance spectroscopy measurements, EIS. In all experiments, the carbon steel electrode was allowed to reach a stable open circuit potential value, E_{corr}. Polarization curves were recorded at a constant sweep rate of 1 mV s^{-1} 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 a saturated calomel electrode (SCE) as reference with a Lugging capillary bridge. Corrosion current density values, I_{corr}, were obtained by using Tafel extrapolation. Electrochemical impedance spectroscopy tests were carried out at E_{corr} by using a signal with 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.

3. RESULTS AND DISCUSSION

The effect of *Alliuym sativum* concentration on the weight loss results for carbon steel in 0.5 M H_2SO_4 at 25, 40 and 60 ^{0}C are given in Fig. 1, where it can be seen that, regardless the testing temperature,' as the inhibitor concentration increases the weight loss decreases, reaching its lowest value with the addition of 400 ppm. With a further increase in the *Alliuym sativum* concentration the weight loss increase once again. Thus, the lowest corrosion rate is reached when 400 ppm of *Alliuym sativum* are added to the environment. It can be seen also that the weight loss increases with increasing the temperature, which might be due to inhibitor degradation with the temperature. Inhibitor

efficiency increases with the inhibitor concentration, reaching its highest value with an inhibitor doses of 400 ppm, Fig. 2, which indicates that the decrease in the corrosion rate is due to the inhibitor adsorption on the steel surface. It is generally accepted that the first step during the adsorption of an organic inhibitor on a metal surface usually involves replacement of water molecules absorbed on the metal surface:

$$Inh_{sol} + xH_2O_{ads} \rightarrow Inh_{ads} + xH_2O_{sol} \quad (3)$$

The inhibitor may then combine with freshly generated Fe^{2+} ions on steel surface, forming metal-inhibitor complexes [28, 29]:

$$Fe \rightarrow Fe^{2+} + 2e \quad (4)$$

$$Fe^{2+} + Inh_{ads} \rightarrow [Fe\text{-}Inh]_{ads}^{2+} \quad (5)$$

The resulting complex, depending on its relative solubility, can either inhibit or catalyze further metal dissolution or increase its corrosion rate.

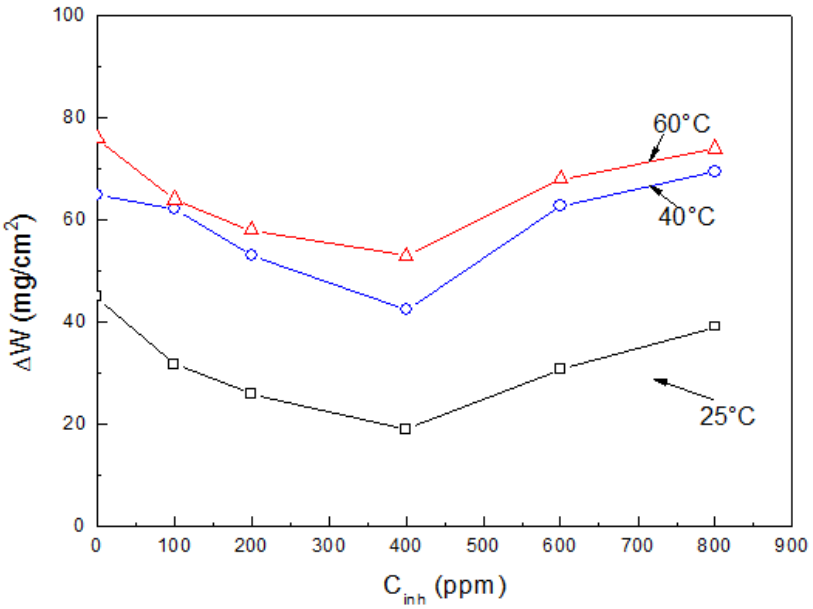

Figure 1. Effect of *Alliuym sativum* concentration on the weight loss measurements for 1018 carbon steel in 0.5 M H_2SO_4 at different temperatures.

At low concentrations the amount of *Alliuym sativum* is insufficient to form a compact complex with the metal ions, so that the resulting adsorbed intermediate will be readily soluble in the acidic environment. But at relatively higher concentrations more *Alliuym sativum* molecules become available for complex formation, which subsequently diminishes the solubility of the surface layer, leading to improve the inhibition of metal corrosion. Since *Alliuym sativum* contains several compounds, mainly allicin and g-glutamylcysteines, these are the primary active compounds responsible for the inhibitive action of garlic.

The apparent activation energy, E_a, associated with 1018 carbon steel in uninhibited and inhibited acid solution was determined by using an Arrhenius-type plot according to the following equation:

$$\log \Delta W = -E_a / 2.303RT + \log F \quad (6)$$

where ΔW is defined in eq. [1], R is the molar gas constant, T is the absolute temperature and F is the frequency factor. Arrhenius plots of (-log ΔW) against 1/T for 1018 carbon steel in 0.5 M H_2SO_4 in absence and presence of *Allium stivum* is shown in Fig. 3. The apparent activation energy obtained for the corrosion process in the free acid solution was found to be 26.1 and 18.46 kJ mol^{-1} in the presence of the inhibitor.

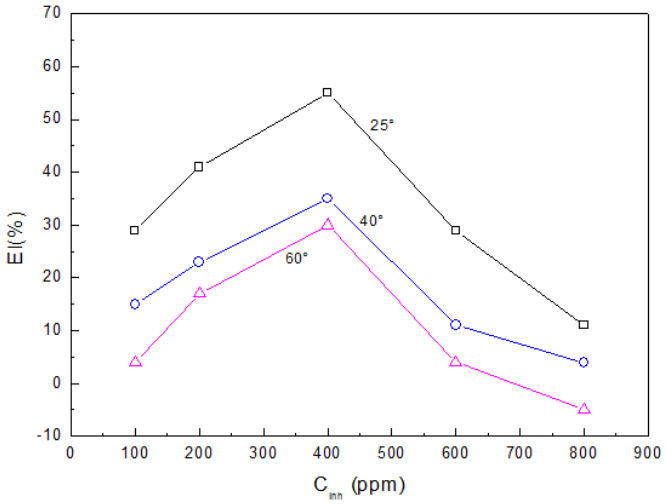

Figure 2. Efficiency values obtained with *Alliuym sativum* on 1018 carbon steel corroded in 0.5 M H_2SO_4 at different temperatures.

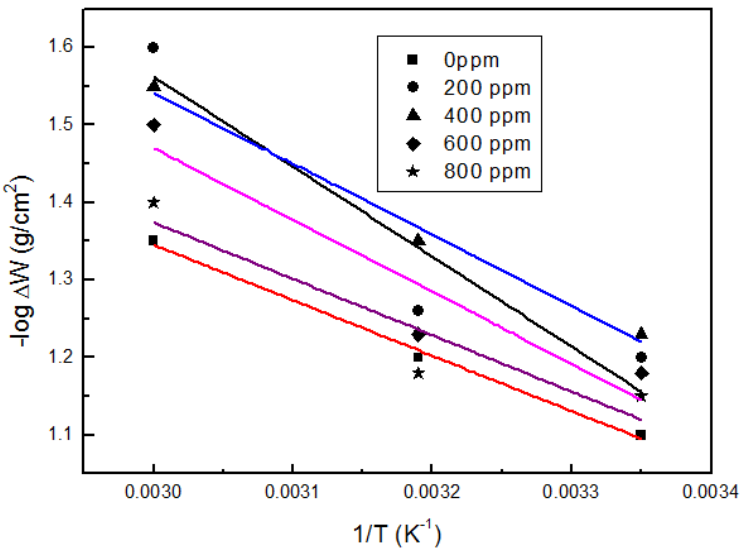

Figure 3. Arrhenius plot for 1018 carbon steel in 0.5 M H_2SO_4 solution containing *Allium sativum*.

Notably, the energy barrier of the corrosion reaction decreased in the presence of the inhibitor, which can be due to the chemisorption of the inhibitor on the steel surface. Actually, it can be concluded that *Allium sativum* can adsorb on the carbon steel surface in two different ways: (i) The *Allium sativum* molecule electrostatically adsorbs onto the anion covered metal surface, through its protonated form, and ii) the *Allium sativum* molecules compete with acid ions for sites at the water covered surface and the unshared electron pairs in nitrogen as well as oxygen may interact with d-orbitals of carbon steel to provide a protective film.

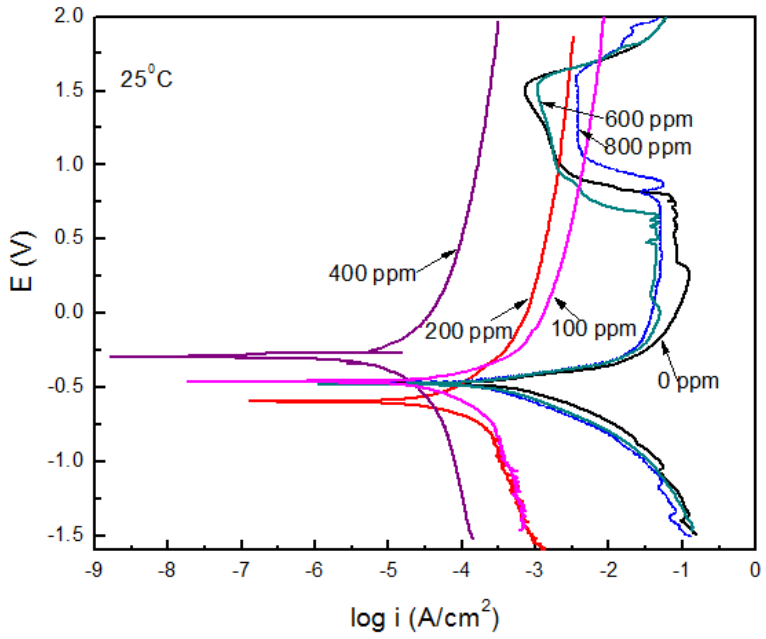

Figure 4. Effect of *Allium sativum* concentration in the polarization curves for 1018 carbon steel in 0.5 M H_2SO_4 at 25^0C.

The polarization curves for carbon steel in 0.5 M H_2SO_4 with the addition of different *Alliuym sativum* concentrations are shown in Fig. 4. This figure shows that in th blank, uninhibited solution, the steel displays an active-passive behavior with an E_{corr} value close to -483 mV and a corrosion current density value around 0.5 mA/cm^2. As the potential is made more anodic, the current density starts to increase untill the formation of a passive layer at a passivation potential,E_{pass}, around 980 mV and an average passive current density value around 1.3 mA/cm^2. With the addition of 100, 200 or 400 ppm of *Alliuym sativum* the I_{corr} value decreases with increasing the inhibitor concentration, but the passive region is lost and an anodic current limit density is observed instead. This limiting anodic current density is due to the formation of corrosion products through which makes more difficult the access of the electrolyte to corrode the underlying metal. With a further increase in the inhibitor concentration, i.e. 600 or 800 ppm, the passive region is displayed once again, but the I_{corr} increases reaching values similar to those found in the uninhibited solution. The I_{pass} values were very similar to that obtained in absence of the inhibitor also. The highest inhibitor efficiency was reached with the addition of 400 ppm. Both the anodic and cathodic Tafel slopes were increased with the addition of *Allium sativum*

when the inhibitor concentration increased up to 400 ppm, table 1, but they were unaffected with a further increase in the inhibitor concentration, which indicates that *Alliym sativum* is a mixed type of inhibitor.

Table 1. Electrochemical parameters obtained from polarization curves at 25 ^{0}C.

C_{inh} (ppm)	E_{corr} (mV)	I_{corr} (mA/cm^2)	I.E. (%)	β_a (mV/dec)	β_c (mV/dec)	E_{pas} (mV)	I_{pas} (mA/cm^2)
0	-480	0.5	----	65	235	980	1.3
100	-460	0.08	84	120	300	----	-----
200	-598	0.06	88	280	358	----	-----
400	-300	0.02	96	390	390	-----	-----
600	-480	0.2	40	70	260	860	1.6
800	-470	0.4	20	65	225	1080	4

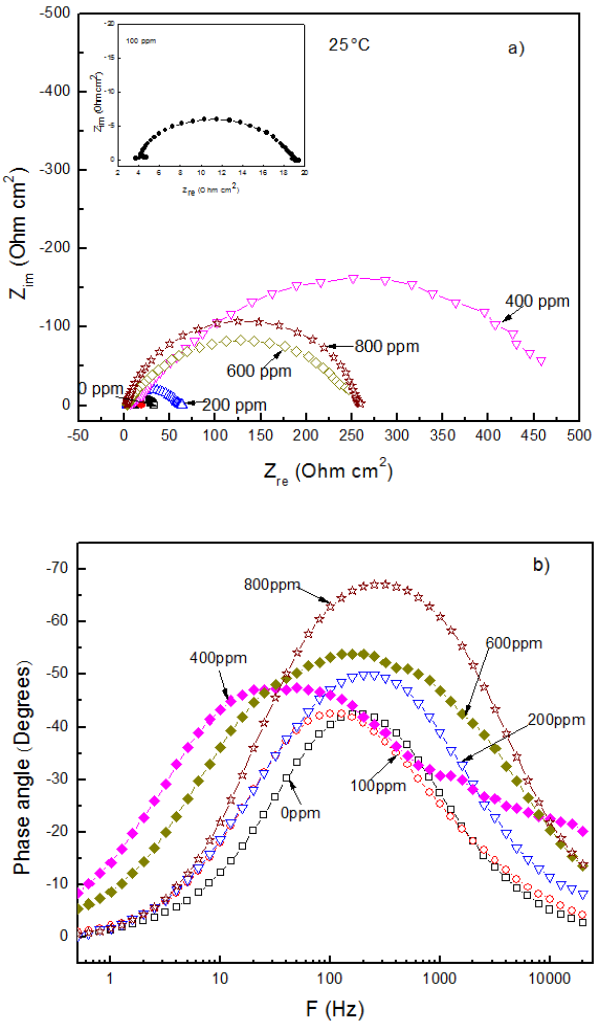

Figure 5. Effect of *Allium sativum* concentration in a) Nyquist and b) Bode plots for 1018 carbon steel in 0.5 M H_2SO_4 at 25^{0}C.

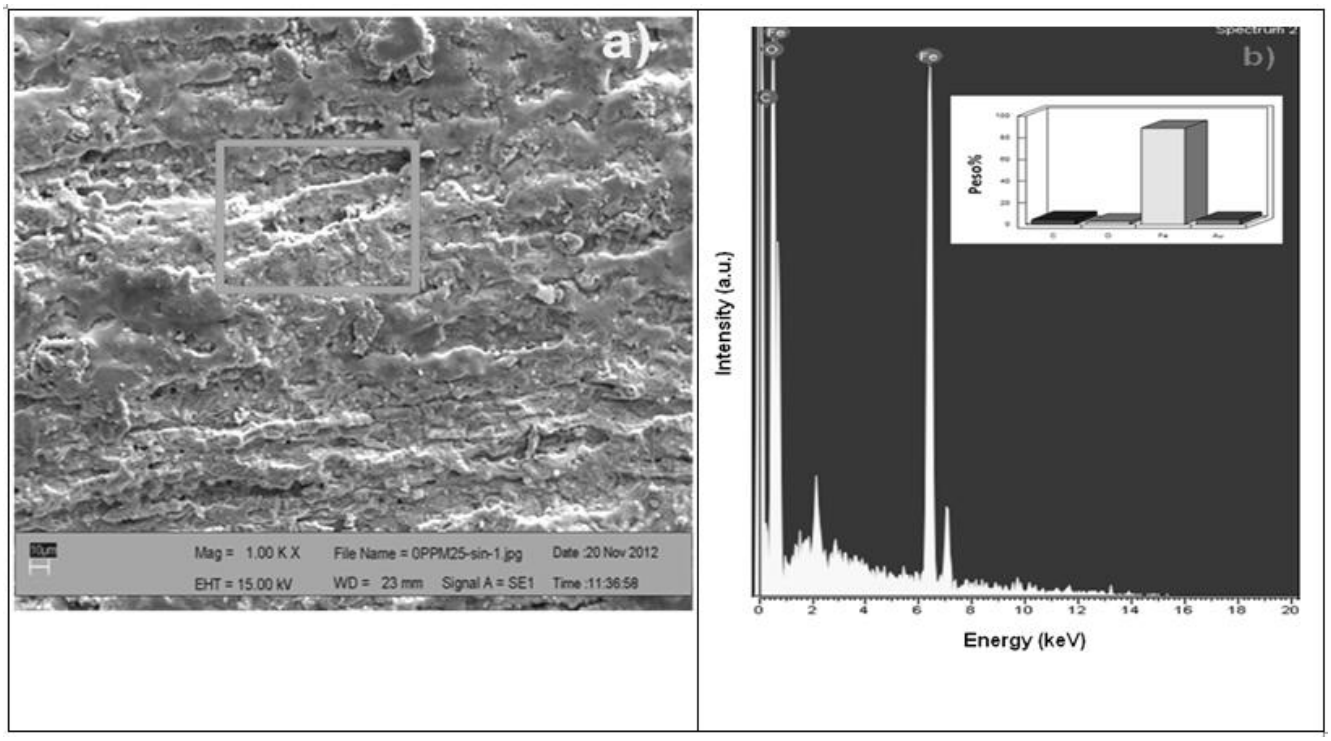

Figure 6. a) Micrographs of 1018 carbon steel corroded in 0.5 M H_2SO_4 solution at 25^0 C containing 0 ppm of *Allium sativum* and b) its microchemical analysis.

The effect of *Allium sativum* concentration on Nyquist and Bode diagrams for carbon steel in in 0.5 M H_2SO_4 at 25 ^{0}C is shown in Fig. 5. Nyquist diagrams show that data display a single capacitive like, deppressed semicircle with its center in the real axis at all frequency values, Fig. 5 a, wich indicate that the corrosion process is under charge transfer control from the steel to the electrolyte through the double electrochemical layer. As the inhibitor concentration increases the semicircle diameter increases reaching its maximum value with the addition of 400 ppm, but it decreases with a further increase in the inhibitor concentration. The semicrcle diameter represents the charge transfer resistance, R_{ct}, eqivalente to the polarization resistance, R_p, inversely proportional to the I_{corr} value. Thus, the highest R_{ct} value obtained with 400 ppm of *Allium sativum* indicates that the I_{corr} value is the lowest at this concentration, increasing with a further increase in the concentration. Bode diagrams, on the other hand, Fig. 5 b, shows only one peak around 100 Hz for the uninhibited solution, which indicates the absence of any protective layer in this case. However, when *Alliuym 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. 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 constants decreases for inhibitor concentrations higher than 400 ppm, indicating that the formed protective layer loses its protectiveness, bringing an increase in the corrosion rate.

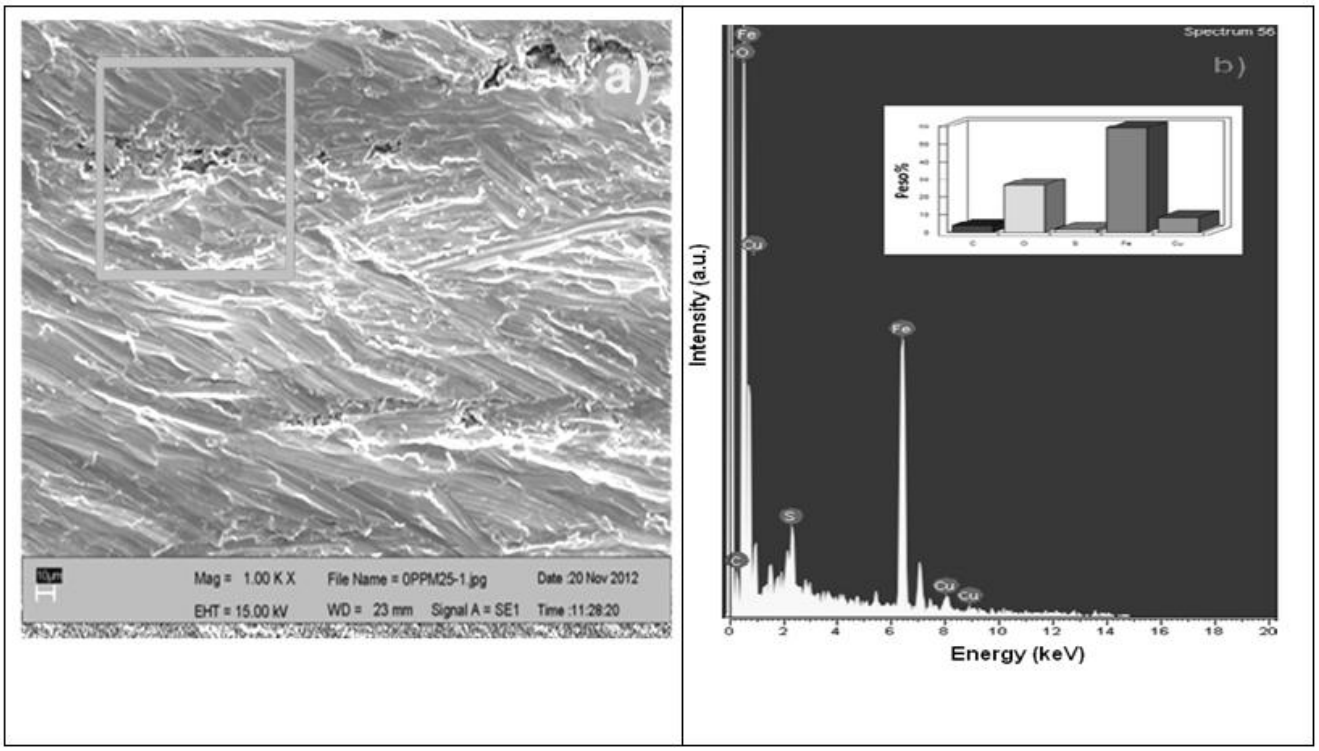

Figure 7. a) Micrographs of 1018 carbon steel corroded in 0.5 M H_2SO_4 solution at 25^0 C containing 400 ppm of *Allium sativum* and b) its microchemical analysis.

To establish whether inhibition is due to the formation of an organic film on the metal surface, scanning electron micrographs were taken. Fig. 6 a, shows the SEM micrograph of the carbon steel surface after of the immersion in 0.5 M H_2SO_4 without corrosion inhibitor together with an EDX microanalysis of the corrosion products, where it can be seen that the steel exposed to the solution without inhibitor forms a porous layer full of micro cracks. The aggressive solution can penetrate through these defects and corrode the underlying metal. However, in presence of inhibitor, Fig. 7 a, the surface has remarkably improved with respect to its smoothness, less porous and micro cracks, indicating considerable reduction of corrosion rate. This improvement in surface morphology is due to the formation of a good protective film on carbon steel surface which is responsible for inhibition of corrosion. Indeed, these pictures show that *Allium sativum* has a strong tendency to adhere to the steel surface and can be regarded as good inhibitor for steel corrosion in normal sulfuric medium. Microanalysis done on the surface of the metal exposed to 0.5 M H_2SO_4 without inhibitor, Fig. 6 b, shows the presence of C, O, Fe and Au, suggesting the formation of a compound including iron oxide/hydroxide and C. The former comes from the use of Au for the preparation of specimens to be seen in the SEM. However, for the specimen corroded in presence of *Allium sativum*, Fig. 7 b, in addition to C, O and Fe, it was found the presence of S from the sulphur-containing constituents in garlic such as allicin, and g-glutamylcysteines.

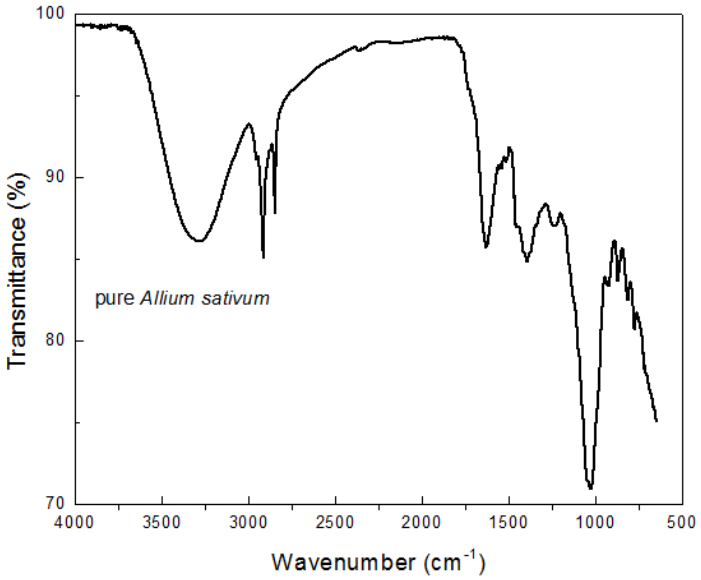

Figure 8. Infrared spectrum of pure hexanic *Allium salivum* extract.

To have some insight of the compounds found in the *Allium sativum* extract, an infrared spectrum was take to the pure extract as well as in the extract+ sulfuric acid before and after the corrosion test. Fig. 8 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 hexanic 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 719 cm^{-1} assigned to C-S bond; a strong signal at 1016 cm^{-1} from sulfoxy (S=O) and the vinyl group appeared at 1123 $cm^{-1}$and at 922 cm^{-1} due to the C=C-H group [30]. Garlic contains at least 33 sulphur compounds which are responsible for both garlic's pungent odor and many biological effects [31]. 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 [32, 33].

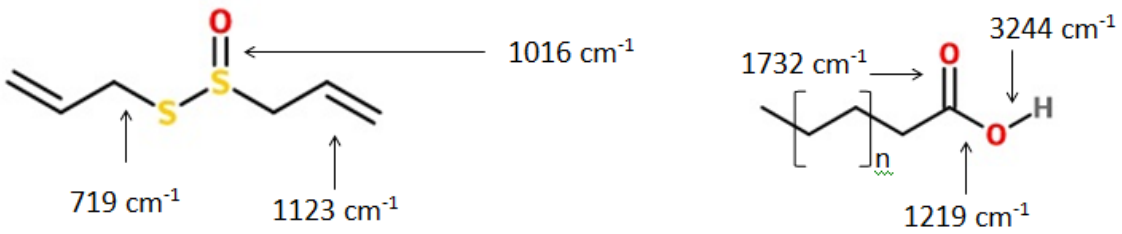

Figure 9. (a) Allicin structure (b) General structure of fatty acid and wave number from representative groups.

The IR information suggests the presence of allicin in the crude hexane extract (Fig. 9 a). 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 (Fig. 9 b) and suggest the presence of them in the hexanic extract of garlic [33, 34]. In the fatty acids structure, -CH_2- groups are present and the scissoring signal from these groups appeared in IR spectrum at 1462 cm^{-1}.

When 400 ppm of *Allium salivum* extract was added to the 0.5 M H_2SO_4 solution, Fig. 10, before the corrosion test, the few signals describe sulphur compounds and the fatty acids were present in the corrosion inhibition system, disulfide bond appeared at 533 cm^{-1}, the sulfoxy group shown at 1074 cm^{-1}, vinylidene group (C=C) appeared at 1181 cm^{-1} and the bond for hydrogen adjacent to vinylidene (H-C=C) appeared at 873 cm^{-1}.

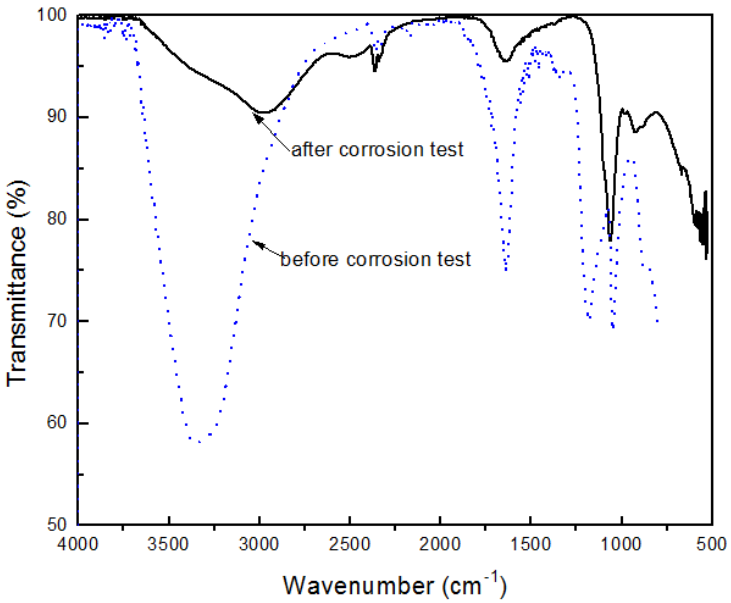

Figure 10. Infrared spectra of the 0.5 M H_2SO_4 + 400 ppm of *Allium salivum* extract solution before and after the corrosion test.

For the fatty acids, at 1635 cm^{-1} carbonyl (C=O) acid group was shown, whereas at 3354 cm^{-1} appeared the signal for hydroxyl (OH) group and at 2970 cm^{-1} the stretching signal for the methylene (-CH_2-) was present. After the corrosion test, a few signals appeared at 2970 cm^{-1} shown the stretching signal for methylene (-CH2-) group and the bond for hydrogen adjacent to vinylidene (H-C=C) appeared at 921 cm^{-1}. At 1635 cm^{-1} the carbonyl (C=O) group appeared, at 1062 cm^{-1} the sulfoxy group was shown and at 529 cm^{-1} the disulfide (S-S) bond appeared. It can be noted that the signal for the hydroxyl (OH) group decreased after the corrosion test, which can be because of the formation of the passive film on the metal maybe due to the formation of FeOH, and a broadening of a band in the 2500-300 cm^{-1} interval. The presence of Fe and O on the protective film was shown in Fig. 7, which supports the idea of the formation of $Fe(OH)_2$ in the passive film for the prevention of corrosion, whereas the presence of S suggests the formation of a complex as indicated in eq. [5]. The high inhibitive performance of this extract suggests a strong bonding of the *Allium sativum* derivatives on

the metal surface due to presence of lone pairs from heteroatom (oxygen) and p-orbitals, blocking the active sites and therefore decreasing the corrosion rate. Therefore, bonding between inhibitor molecules onto carbon steel surface occurs through sharing electrons of the OH group present in the allicin molecule of the pure extract and vacant d-orbitals of iron.

4. CONCLUSIONS

The possibility of using *Allium sativum* extract as corrosion inhibitor for 1018 carbon steel in 0.5 M H_2SO_4 has been evaluated. *Allium sativum* was proved to be a good inhibitor with its efficiency increasing as the concentration increased up to 400 ppm. Higher or lower inhibitor concentrations increased the corrosion rate and decreased its efficiency. The decrease in the corrosion rate by *Allium sativum* extract was due to the formation of a protective external film which contained compounds present in the garlic extract. *Allium sativum* acted mainly as a mixed type of inhibitor which was chemisorbed on the steel surface.

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