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Influence of the Inhibition of Corrosion of S235 Steel in a Solution of Perchloric Acid by Gum Arabic

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Abstract The behavior of S235 metal, a general purpose metal construction material in Senegal, has been studied in perchloric acid solution in the presence of gum arabic from Senegal as a corrosion inhibitor. The protective power of this compound has been evaluated by electrochemical methods (stationary polarization curves and electrochemical impedance spectroscopy), at different inhibitor contents. We have considered testing gum arabic as an aqueous corrosion inhibitor. Electrochemical tests show that the values of the corrosion parameters vary with the content of gum arabic. An optimal inhibitory efficacy of approximately 88% is obtained for this substance, thus demonstrating the inhibitory nature.

Keywords: *corrosion, gum arabic, S235 steel, perchloric acid*

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1. Introduction

Corrosion is a harmful phenomenon that affects all kinds of materials (metals, ceramics, polymers) in various environments (aqueous media, atmosphere, high temperatures) [1,2]. Corrosion phenomena depend on a large number of factors such as: the nature and structure of the material, surface treatments (mechanical, chemical, electrochemical, etc.), the environment and its chemical characteristics, temperature, microorganisms, the hydrodynamic regime to which the material is subjected and the constraints which are imposed on it.

Corrosion of a metal in aqueous environments results from oxidation but not necessarily due to the oxygen dissolved in the water. Oxidation can also occur when other chemical species, especially particularly aggressive ions are present (chloride, sulfate, nitrate, ammonium, carbonate ...). This is how organic inhibitors, based on sodium benzoate and other salts of substituted aromatic acids and fatty acids have been proposed by Kuznetsov et al. [3,4,5,6]. Most of these inhibitors have been shown to be effective from a certain "critical minimum concentration" [7]. More recently, certain minerals are increasingly used as inhibitors of steel corrosion. These are different classes of clays used in the form of nanocomposites incorporated into coatings [8,9]. Natural clays have been used as an ecological inhibitor [10]. Due to the new directives on environmental protection, natural inhibitors such as gum arabic are by far the most suitable for the benefit of other mineral inhibitors than organic. The mineral inhibitors are generally chromates and nitrites which are considered toxic and carcinogenic. Several studies have shown that the gum arabic behaves as an effective inhibitor for carbon steel in a hydrochloric acid solution [11]. The inhibitory efficacy of gum arabic has also been studied in sulfuric acid [12,13]. A synergistic study of gum arabic and potassium iodide for the corrosion of carbon steel in sulfuric acid has given very good inhibitory efficacy [14].

Our present study consists in studying the corrosion behavior of the general construction metal, S235, widely used in Senegal. The objective is to establish the ability of gum arabic to effectively inhibit the corrosion of building material S235 in a 1 M solution of perchloric acid ($HClO_4$).

2. Experimental Conditions and Methods

We used S235 steel, supplied by the Industrial Development Center of Senegal (IDC). Remember, S235 steel is a building material with the conventional minimum yield strength 235 N/mm^2 or (Mpa). Its centesimal chemical composition is indicated in Table 1. The steel was cut using a Gruchoir universal shear, in the form of plates with a surface area of 3.6 cm^2.

The electrochemical measurements were carried out on samples coated in "Epoxy Steel" type resins.

Table 1. Chemical composition of steel, as a percentage of elements other than iron [15]

Designation	C	Mn	N	P	S	Cu
S235	0.17	1.40	0.012	0.04	0.04	0.55

Before each test, the sample undergoes a pretreatment, which consists of polishing the surface of the metal with sandpaper of increasingly fine particle size (180-320-400-600-1200) followed by rinsing with distilled water and drying in the open air.

The electrolyte used is a solution of perchloric acid $HClO_4$ with a concentration of 1 M. This electrolyte is obtained by diluting in distilled water a commercial solution of perchloric acid whose mass percentage is 70% and density 1.68.

For each test, an amount of gum arabic ranging from 0% to 0.6% is added relative to the volume of acid used to monitor the behavior of the metal and the inhibitory effectiveness.

The inhibitor used for this study is gum arabic. A natural product, *Acacia senegal*, very abundant in the south and east of Senegal. Gum arabic is a complex polysaccharide which is in the form of a branched chain. It's a compound; either neutral or slightly acidic, which is in the form of a mixed salt (calcium, magnesium and potassium) of polysaccharidic acid. Figure 1 shows the molecular structure of gum arabic [16].

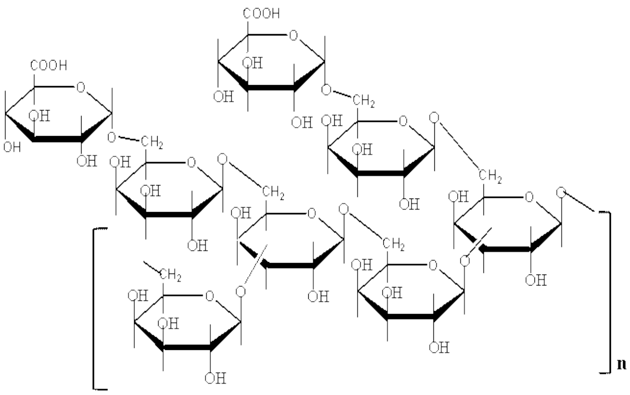

Figure 1. Chemical structure of gum arabic

The electrochemical measurements were carried out using a three-electrode assembly: a platinum grid as a counter electrode, an Ag / AgCl reference electrode and the working electrode made up of the sample. The different experimental measurements are carried out using a palmsens 4 potentiostat controlled by the PSTrace 4.8 software.

The corrosion of S235 metal and the effectiveness of gum arabic were studied by the potentiodynamic method, the scanning speed being fixed at 0.5 mV / s and the equilibrium time 300 seconds. The working electrode is kept immersed beforehand at the free corrosion potential for one hour with magnetic stirring. The determination of the electrochemical parameters (i_{corr}, E_{corr}, R_p, b_a and b_c) from the Tafel polarization curves, is done using a non-linear regression by the PSTrace 4.8 software, according to the Stern equation. Geary after correction of the ohmic drop. The inhibitory efficacy is calculated from the following formula [17];

$$IE = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \qquad (1)$$

i^0_{corr} and i_{corr} being the corrosion current densities without and with inhibitor, respectively.

In the same way as the potentiodynamic method, the plotting of the electrochemical impedance diagrams was carried out using the PSTrace 4.8 software with a signal amplitude of 10 mV. The frequency range explored varies from 5000 Hz to 100 mHz. The inhibitory efficacy was evaluated using the equation [17];

$$IE = \frac{R_P - R_P^0}{R_P} \times 100 \qquad (2)$$

R_P and R_P^0 representing the charge transfer resistance in the absence and in the presence of inhibitor, respectively.

3. Results and Discussion

3.1. Monitoring of Abandonment Potentials

The evolution of the free potential or the potential for abandonment during a corrosion test is a first clue to estimate the possible gravity of the degradation during the immersion of the metal. The sample is immersed in the solution and the potential for free corrosion of the working electrode is measured as a function of time during the duration of the immersion. Its evolution provides information on the processes taking place at the metal/electrolyte interface. This allows to assess the stationarity of the corrosive system. Figure 3 represents the plots of the abandonment potentials of the metal S235 in the corrosive medium of perchloric acid without and with gum arabic of variable propositions from 0.05% to 0.6%.

These results clearly show the effect of the concentration of the inhibitor on the corrosion potential. We calculated the difference between the corrosion potentials in the presence and in the absence of inhibitor (ΔE) grouped in Table 2. It can be seen that ΔE is positive, whatever the inhibitor content. Corrosion potentials are therefore slightly shifted to more anodic month values with the addition of the inhibitor.

Gum arabic therefore appears to be a mixed inhibitor. ΔE increases with the inhibitor content up to the optimal value of 12.20 mV and decreases beyond.

The results of the various dropout potential measurements show that the attack or dissolution of the steel is more intense in the solution without inhibitor.

The potential for free corrosion decreases during the first few minutes, which may be due to the dissolution of an oxide film formed on the surface [18].

Table 2. Corrosion potential E_{corr} (V / Ag / AgCl) measured of S235 steel in perchloric acid (1 M) at different concentrations of inhibitors

Inhibitor content (%)	0	0.05	0.1	0.2	0.3	0.4	0.5	0.6
E_{corr} (mV/Ag/AgCl)	-0,42885	-0,42417	-0,42053	-0,41948	-0,4171	-0,41665	-0,41954	-0,42006
ΔE (mV)	0	4,68	8,32	9,37	11,75	12,20	9,31	8,79

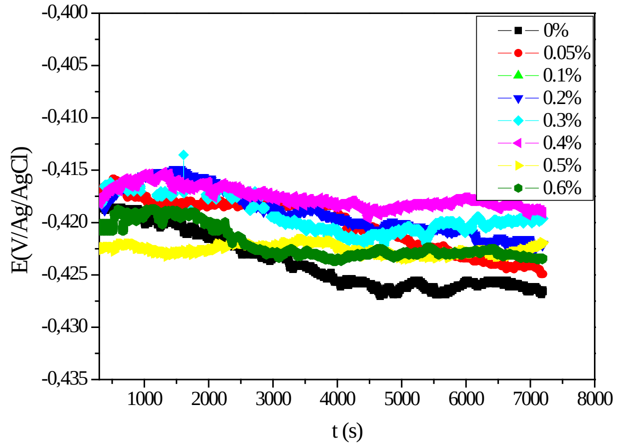

Figure 2. Monitoring of the corrosion potential of S235 steel in $HClO_4$ at different concentrations of gum arabic

It also appears that the final potential increases with the inhibitor content, but seems to decrease after a certain inhibitor content: 0.4%. At this optimum content, the protective film is probably deposited on the steel, which automatically leads to the same reduction in corrosion. Figure 2 also shows that the inhibition reaches its maximum value at 0.4%.

3.2. Polarization Curves

It is clear from the free corrosion potential monitoring curves that the abandonment potentials stabilize after 25 to 40 min of immersion for all concentrations. We have therefore chosen an equilibrium time of 30 minutes for the polarization measurements.

The stationary polarization curves, in the absence and in the presence of the different inhibitor concentrations are represented in Figure 3.

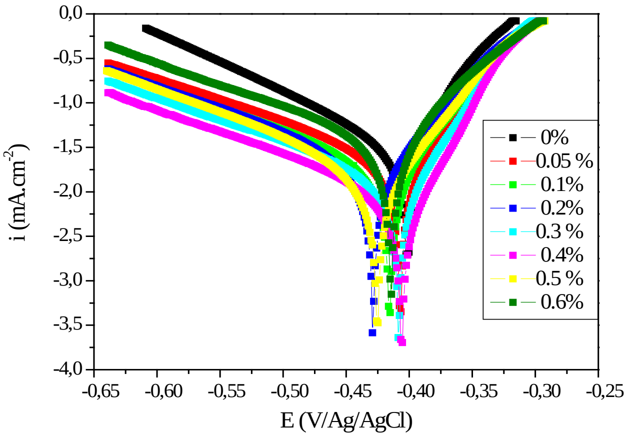

Figure 3. Stationary polarization curves of S235 steel in $HClO_4$ (1M), at different concentrations of gum arabic inhibitor

It can be seen that there is a small variation in the corrosion potential as a function of the concentration of the inhibitor. The inhibitory nature of gum arabic is therefore mixed. Indeed, it is established that an inhibitor can be classified as cathodic or anodic type if the displacement in E_{corr} during the addition of the inhibitor is greater than 85mV compared to the corrosion potential of steel in uninhibited medium [19,20]. On the other hand for our study, the maximum displacement is 22 mV.

The experimental results also show that there is a slight displacement of b_c and b_a in the $HClO_4$ solution (1M). It can therefore be suggested that the mechanism of corrosion has not changed with the addition of the inhibitor [21].

We also note that the cathode Tafel lines are parallel, thus indicating that the process follows a charge transfer mechanism [22].

The introduction of the inhibitor into the perchloric acid solution does not modify the mechanism of evolution and reduction of hydrogen on the surface of the steel.

The strong decrease in current density respectively without the inhibitor (574 µA / cm^2) and with 0.4% of this product (79 µA / cm^2) is due to an inhibiting activity of gum arabic on the steel interface.

The inhibitory power increases with the concentration of the substances and reaches a maximum value of 86.23% for a content of 0.4% in gum arabic. This inhibition rate is very satisfactory and modifies the electrochemical behavior of steel in the vicinity of E_{corr}. All the electrochemical parameters drawn from these curves are grouped in Table 3.

Table 3. Electrochemical parameters from intensity-potential curves of steel in the absence and in the presence of gum arabic

C (%)	E_{corr} (mV)	i_{corr} (µA/cm^2)	R_p (Ω)	b_a (mV/dec)	b_c (mV/dec)	V_{corr} (mm/year)	IE (%)
0	-0.400	574	35	66	151	3.43	
0.05	-0.410	141	131.	60	149	0.872	75.43
0.1	-0.415	105	180	62	147	0.674	81.67
0.2	-0.431	102	187	60	150	0.637	82.22
0.3	-0.408	82.5	198	50	151	0.553	85.62
0.4	-0.407	79	202	49	151	0.507	86.23
0.5	-0.419	86	190	50	153	0.615	85.05
0.6	-0.414	153	104	48	156	1.08	73.34

Gum arabic is a highly water-soluble polysaccharide, containing a hydroxyl functional group (-OH), and a carboxyl functional group (-COOH) [23].

In an acid solution such as 1M perchloric acid solution ($HClO_4$), the carbonyl compound (C = O) can be protonated and the molecule then exists in the form of polycation. The anions of ClO_4^- tend to be adsorbed on the surface of the steel, which leads to a negative charge on the surface of the steel. The formation of positively charged protonated species facilitates the adsorption of the compound on the surface of the metal by the electrostatic interaction between the gum arabic molecule and the surface of the steel (physisorption).

3.3. Electrochemical Impedance Spectroscopy (EIS)

We have also studied the corrosion of the S235 material by SIE, in the presence and absence of gum arabic. Figure 4 and Figure 5 represent the electrochemical impedance diagrams respectively in the Nyquist and Bode plan of the steel in the solution of perchloric acid ($HClO_4$ at 1 M) with different inhibitor proportions, recorded after 2 h of immersion at room temperature at the abandonment potential in the frequency range from 5000 Hz to 100 mHz.

In the Nyquist plan, the impedance diagrams in the presence of an inhibitor show the appearance of two indistinguishable capacitive loops with a significant increase in the bias resistance. At high frequencies, the size of the capacitive loop increases with concentration the gum arabic. This is attributed to the formation of an inhibitor film which has a barrier effect against aggressive ions [24].

At low frequencies, the addition of the inhibitor causes an increase in the value of the polarization resistance R_P (the size of the loop between the high frequency and the low frequency) which presents a non-monotonic variation as a function of the content of inhibitor. The highest value is obtained for 0.4% (192.24 $\Omega.cm^2$) (Table 4). This can be attributed to load transfer [25].

Table 4. Results of EIS measurements with the potential for abandonment in the absence and presence of gum arabic

C (%)	R_s ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	C_{dL} ($\mu F.cm^{-2}$)	EI **(%)**
0	2.85	25.32	235	0.00
0.05	3.47	118.16	84.34	78.54
0.1	3.62	127.38	69.65	80.12
0.2	3.20	137.30	55.14	81.73
0.3	3.45	185.73	31.5	86.43
0.4	3.82	192.24	24.3	87.62
0.5	3.90	171.21	38.80	85.19
0.6	4.02	88.21	150	71.21

The decrease in the double layer capacity (C_{dl}) from 235 to 24 $\mu F.cm^{-2}$, is explained by a decrease in the local dielectric constant and / or an increase in the thickness of the electric double layer, resulting from the adsorption of gum arabic molecules on the metal interface.

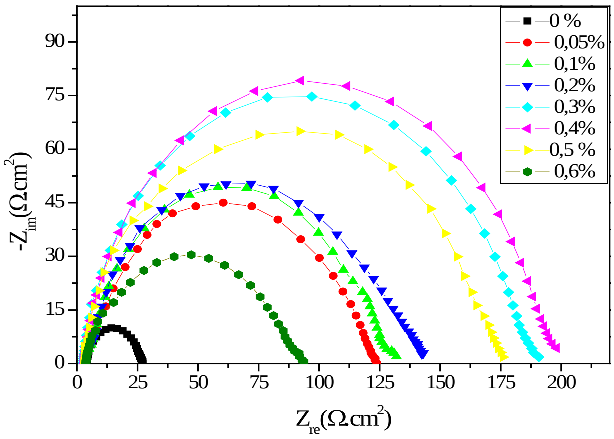

Figure 4. Nyquist diagrams of corrosion of S235 steel in 1M $HClO_4$ acid at different concentrations of gum Arabic

Bode diagrams (Figure 5a) indicate the existence of an equivalent circuit containing a single element of constant phase in the metal / solution interface. The increase in absolute impedance at low frequencies in the Bode diagrams confirms that protection is better at high concentrations of the inhibitor. The observation of a single phase peak (Figure 5b) in the center frequency range shows the existence of a single constant, linked with the electric double layer [26].

Table 4 also shows that the transfer resistance increases up to the content of 0.4 % of gum arabic. At this concentration, the charge transfer resistance (R_{ct}) is 192.24 $\Omega.cm^{-2}$ and an inhibitory efficiency (IE) of 87.62 %. Beyond this content, the inhibitory power decreases as the amount of gum arabic increases.

The equivalent circuit (Figure 6) includes an electrolytic resistor (Rs), a charge transfer resistor (R_{ct}) and a constant phase element (CPE) [27]. The parameter CPE replaces the capacity of the double layer (C_{dl}) in order to give a more precise adjustment to the experimental results [28].

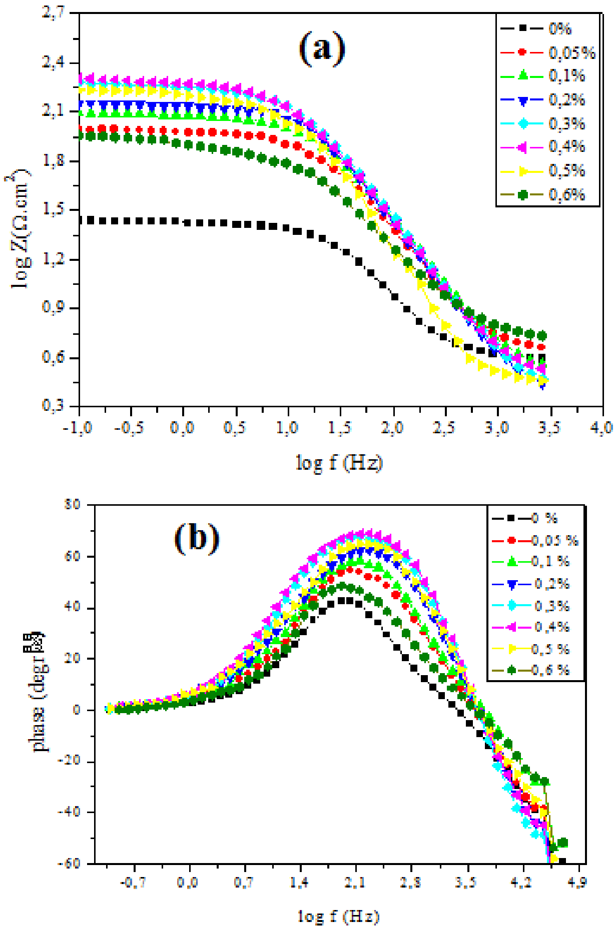

Figure 5. Bode curves (a) and phase angle (b) of the corrosion of S235 steel in 1 M $HClO_4$ at different concentrations of gum arabic

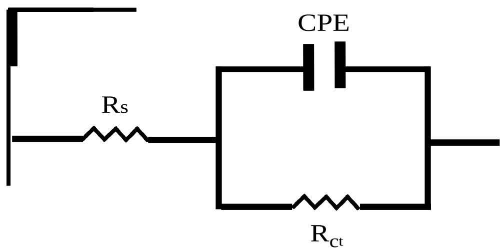

Figure 6: Electrical circuit for modeling the impedance spectra

4. Conclusion

During this work, we studied the influence of corrosion inhibition of S235 steel in a solution of perchloric acid ($HClO_4$) of 1M concentration in order to protect installations against corrosion. This study was carried out electrochemically.

Corrodability tests were performed by monitoring the free corrosion potential, Tafel polarization and by electrochemical impedance spectroscopy measurements. Measurements by monitoring the corrosion potential show a permanent attack on the steel in the absence of gum arabic and for a certain content in the presence of the inhibitor. The study also showed that the rate of corrosion is reduced by about 88% through the use of a natural inhibitor, gum arabic. The results obtained show that this inhibitor acts as a mixed inhibitor and has an efficiency of the order of 88% for an optimal concentration of 0.4%. The evolution of the impedance diagrams in the Nyquist plane as a function of the concentrations of natural inhibitor confirms the formation of a protective layer, which results in the increase in the charge transfer resistance together with a decrease in the capacity of double layer. The results obtained by the Tafel method are in agreement with those obtained by electrochemical impedance spectroscopy measurements with an inhibitory efficiency of the order of 88% to 0.4% of gum arabic.

References

[1] M. G. Fontana, "Corrosion engineering", *Mc Graw-Hill. Book. Company*, N.Y. 1986.

[2] D. landolt, "Traité de matériaux", France, 1993.

[3] Kuznetsov Y.I., "Organic Inhibitors of Corrosion of Metals", *Plenum Press*, New York, 1996.

[4] Kuznetsov YU, Andreev NN. "The Effect of Salts of Substituted Benzoic Acids on the Local Dissolving of Metals". *Zashch. Met*., 23(3):495-498.), 1987

[5] Kuznetsov JI. "Rol kompleksovanija w ingibirovanii korozji". *Zaščita Metallov.*, 26(6), 954-964, 1990.

[6] N.N. Andreev, S.V. Lapshina, Y.I. Kuznetsov, *Zastchita. Met*., 28. 1017, 1992.

[7] Reinhard G, Radtke M, Rammelt U. "On the role of the salts of weak acids in the chemical passivation of iron and steel in aqueous solutions". *Corrosion science*, 33(2), 307-313, February 1992.

[8] Navarchian AH, Joulazadeh M, Karimi F. "Investigation of corrosion protection performance of epoxy coatings modified by polyaniline/clay nanocomposites on steel surfaces". *Progress in Organic Coatings*, 77(2), 347-353, February 2014.

[9] Motte C, Poelman M, Roobroeck A, Fedel M, Deflorian F, Olivier MG. "Improvement of corrosion protection offered to galvanized steel by incorporation of lanthanide modified nanoclays in silane layer". *Progress in Organic Coatings*, 74(2), 326-333, Jun 2012.

[10] Diadioly GASSAMA, Modou FALL, Ismaïla YADE, Serigne Massamba SECK, Mababa DIAGNE and Mouhamadou Bassir DIOP, "Clays Valorization as Corrosion Inhibitors for E400 Reinforcing Steel", *Ovidius University Annals of Chemistry, 27(1), 28-35*, 2016.

[11] Bentrah, H., Rahali, Y., & Chala, A. (2014). "*Gum Arabic as an eco-friendly inhibitor for API 5L X42 pipeline steel in HCl medium*". *Corrosion Science*, 82, 426-431.

[12] S.A. Umoren, O. Ogbobe, I.O. Igwe, E.E. Ebenso, "Inhibition of mild steel corrosion in acidic medium using synthetic and naturally occurring polymers and synergistic halide additives", *Corros. Sci* 50, 1998-2006, 2008.

[13] S.A. Umoren, "Inhibition of aluminium and mild steel corrosion in acidic medium using Gum Arabic", *Cellulose* 15, 751-761, 2008.

[14] Djellab M, Bentrah H, Chala A, Taoui H. "Synergistic effect of halide ions and gum arabic for the corrosion inhibition of API5LX70 pipeline steel in H_2SO_4". *Materials and Corrosion*, 1-12, 2018.

[15] N. Gilbert, "Structural Steel-S235 chemical composition, mechanical properties and common applications". Azom. com [online], 2012.

[16] M. Doubi, A. Dermaj, H. Ramli, D. Chebabe, N. Hajjaji, A. Srhir, "Inhibition de la corrosion d'un acier E24 dans des eaux d'irrigation agricole", *ScienceLib Editions Mersenne, Mersenn*e, 5 (130110) ISSN, 2111-4706, 2013.

[17] S. A. Umoren M. M. Solomon, vEffect of halide ions on the corrosion inhibition efficiency of different organic species" - *A review. Journal of Industrial and Engineering Chemistry*, 21, 81-100, 2015.

[18] O.Sihem, "infuence des inhibiteurs sur la corrosion sur la corrosion de a37 dans diférents milieux et leurs effets bioacides sur e. coll", *Thèse université BADJI MAKHTAR-ANNABA*, 2013.

[19] M. Sherif El-Sayed, J.H. Potgieter, J.D. Comins, L. Cornish, P.A. Olubambi, C.N. Machio, *Corros. Sci.*, 51, 1364, 2009.

[20] X. Li, S. Deng H. Fu, "Synergism between red tetrazolium and uracil on the corrosion of cold rolled steel in H_2SO_4 solution". *Corrosion Science*, 51(6), 1344-1355, 2009.

[21] E. S. Ferreira, C. Giacomelli, F. C. Giacomelli A. Spinelli, "Evaluation of the inhibitor effect of l-ascorbic acid on the corrosion of mild steel". *Materials Chemistry and Physics*, 83(1), 129-134, 2004.

[22] X. Li, S. Deng H. Fu, "Triazolyl blue tetrazolium bromide as a novel corrosion inhibitor for steel in HCl and H_2SO_4 solutions". *Corrosion Science*, 53(1), 302-309, 2011.

[23] H.H. Uhlig & H.P. Leckie, *J. Electrochem. Soc*. 12, 262, 1966.

[24] Afia L, Salghi R, Zarrouk A, Zarrok H, Benali O, Hammouti B, Al-Deyab SS, Chakir A, Bazzi L. "Inhibitive action of argan press cake extract on the corrosion of steel in acidic media". *Portugaliae Electrochimica Acta*., 30(4), 267-279, Jul 2012.

[25] Touir R., Dkhireche N., Ebn Touhami M., Sfaira M., Senhaji O., Robind J.J., Boutevin B. Cherkaoui M., "Study of phosphonate addition and hydrodynamic conditions on ordinary steel corrosion inhibition in simulated cooling water", *Mater. Chem. Phys*., 122, 1-9, 2010.

[26] Srisuwan N., Ochoa N., Pebere N., Tribollet B., "Variation of carbon steel corrosion rate with flow conditions in the presence of an inhibitive formulation", *Corros. Sci*., 50, 1245-1250, 2008.

[27] Mohan R, Joseph A. "Corrosion protection of mild steel in hydrochloric acid up to 313 K using propyl benzimidazole: electroanalytical, adsorption and quantum chemical studies". *Egyptian Journal of Petroleum*. 27(1), 11- 20, March 2018.

[28] El Bakri Y, El Aoufir Y, Bourazmi H, Harmaoui A, Sebhaoui J, Tabyaoui M, Guenbour A, Oudda H, Lgaz H, El Hajaji F, Ali AB. "Corrosion control of carbon steel inphosphoric acid by 6-methyl-7H-1, 2, 4-triazolo [4, 3-b][1, 2, 4]-triazepine-8 (9H)-thione: Electrochemical studies". *Journal of Materials*, 8(8), 2657-2666, 2017.