

Kinetics and Thermodynamic Study of Inhibition Potentials by 3-Acétyl-4-Oxo-Benzopyranone on Mild Steel in H₂SO₄ Solution and Synergistic Effect of Chloride Ions

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ABSTRACT: The effects of single 3-Acétyl-4-oxo-benzopyranone (ACBP) and the mixture of various concentrations of 3-Acétyl-4-oxo-benzopyranone ACBP and 0.02M NaCl on the corrosion of mild steel in 0.5M sulfuric acid have been investigated by using weight loss method. This study revealed that mild steel in sulfuric acid has been more efficiently inhibited by ACBP in the presence of NaCl than single ACBP, and inhibition efficiency increases with increasing concentration of ACBP at the same temperature, but decreases with increasing temperature studied. A synergistic effect exists when ACBP and chloride ion are used together to prevent mild steel corrosion in 0.5M sulfuric acid at every experimental temperature. The adsorption of ACBP and ACBP+ NaCl on the mild steel surface obeys Langmuir and Frumkin adsorption isotherm respectively. Some thermodynamic parameters such as adsorption heat, adsorption entropy and adsorption free energy have been calculated by employing thermodynamic equations. Kinetic parameters such as apparent activation energy and pre-exponential factor have been calculated and discussed.

KEYWORDS: 3-Acétyl-4-oxo-benzopyranone; Halide ions; Inhibition efficiency; Synergistic effect; Langmuir Frumkin and Temkin adsorption isotherm.

I. INTRODUCTION

Acid solutions of various concentrations are extensively used in many industrial processes. Corrosion is an afflicting problem associated with every use of metals. Corrosion is an important problem resulting in the production of waste with great toxicity and loss of resources and money during these applications. Mild steels undergo considerable dissolution when they are exposed to acid solutions or aggressive environments. A survey of literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acidic media has been recognized for a long time [1-5]. Among various organic inhibitors, organic compounds containing heteroatom are popularly used as corrosion inhibitors of mild steel in acid media [6-12]. The protective action of an inhibitor in metal corrosion is often associated with chemical or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other. It has been observed that adsorption depends on the chemical structure of molecules, electron density at the donor atom, π -orbital character, the chemical composition of solutions. Synergistic

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effects describe the increase in the effectiveness of a corrosion inhibitor in the presence of another substance in the corrosive medium. This phenomenon has been frequently used in practice [13-16]. Furthermore, several studies have reported the synergism existing between an organic molecule and halide ions. Hence, the presence of halide ions in acidic media synergistically increases the adsorption ability of some organic compounds and the synergism is often more pronounced in the presence of iodide ions. The pronounced synergistic action is due to the larger ionic radii, high hydrophobicity, and low electronegativity of iodide ions compared to other halide ions [17-20]. The aim of this study was to investigate the corrosion inhibition action 3-Acetyl-4-oxo-benzopyranone ACBP on mild steel corrosion in 0.5 M H₂SO₄ solution. Then, we attempted to increase the inhibition efficiency synergistically further by the chloride ions addition to the Acetyloxobenzopyranone containing corrosive solution.

II. EXPERIMENTAL PROCEDURES

II.1. Organic Compound

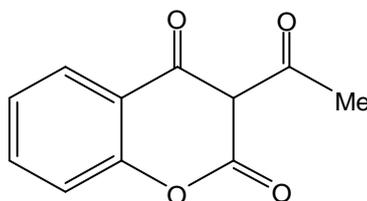


Figure 1: The chemical structure of 3-Acetyl-4-oxo-benzopyranone (ACBP)

ACBP white solid, m.p.134°-136°C. IR: ν_{CO} (lactone α, β -insaturated) = 1732 cm⁻¹, ν_{CO} (ketone α, β -insaturated) = 1674 cm⁻¹. ¹H-NMR (DMSO-*d*₆): δ = 7,3-8,3 ; massif ; 4 H aromatic ; δ =2,8 ; singlet; 3 H. ¹³C-NMR (DMSO-*d*₆): δ_{CO} (ketone) = 162, 4 ppm, δ_{CO} (lactone) = 157, 4 ppm. 3-Acetyl-4-oxo-benzopyranone (ACBP) contains four heteroatoms (oxygen) as well as π electrons, which are assumed to be active centers of adsorption.

II.2. Materials

Tests were performed on a mild steel electrode of the following composition, presented in table 1

Table 1. Chemical composition (wt. %) of mild steel

Element	wt. %
C	0,21
Si	0,38
P	0,09
S	0,05
Mn	0,05
Al	0,01
Fe	Balance

II.3. Solutions

The corrosive medium (0.5 M H₂SO₄) was prepared from AR grade 98% H₂SO₄ using double-distilled water. 1: 3-Acetyl-4-hydroxycoumarine was synthesized in our laboratory and its chemical structure is as shown in Figure 1. The desired concentrations of ACBP solutions (0.001; 0.002; 0.003; 0.004; 0.005 and 0.01M) in presence of 0.02 M were obtained by adding a specified amount of 3-Acetyl-4-oxo-benzopyranone and AR grade NaCl to 0.5 M H₂SO₄ solution separately. The combined inhibitor (ACBP + NaCl) solutions were prepared by adding the required amount of NaCl to ACBP -H₂SO₄ solution. Each experiment was carried out in aerated and stagnant solutions.

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II.4. Gravimetric Technique

Gravimetric method is indeed the most simple and reliable method for the determination of inhibition efficiency. The mild steel sheets of 3,5cm × 1cm × 0.1cm were abraded with a series of emery paper (grade 320-500-800) and washed thoroughly with triple distilled water, degreased with acetone and dried using air flow at room temperature. After weighing accurately, the specimens were immersed in 30 ml beaker, which contained 30 ml sulfuric acid with and without addition of different concentrations of coumarine. All the aggressive acid solutions were open to air. After 6 h at 298° K, the specimens were taken out, washed, dried, and weighed accurately. Experiments were carried out in triplicate. The average weight loss of three parallel mild steel sheets could be obtained. Then the tests were repeated at different temperatures and 0.5 M H₂SO₄ concentration and mass loss was expressed in mg and corrosion rate in mg cm⁻² h⁻¹.

III. RESULTS AND DISCUSSION

III.1 Weight loss and inhibition efficiency

Weight loss is a non-electrochemical technique for the determination of inhibitor efficiency which provides more reliable results than electrochemical techniques because the experimental conditions have been done in a more realistic manner. The loss in weight of carbon steel strips in 1 M H₂SO₄ solution in absence and presence of different concentrations of coumarine during 6 hours of the trials has been determined.

The protection efficiency (*I*%) and the parameter (*θ*) that represents the weight of the metal surface covered by inhibitor molecules were calculated using the following equations [21-23]:

$$I \% = \left(1 - \frac{w_i}{w_o}\right) \times 100 \quad (1)$$

$$\theta = \left(1 - \frac{w_i}{w_o}\right) \quad (2)$$

Where *W_i* and *W₀* are the weight losses in grams of the coupon in the presence and absence of the inhibitor respectively. The corrosion rate of the metal was determined for the immersion period from weight loss through equation (3):

$$\text{Corrosion rate} = \frac{W}{St} \quad (3)$$

Where *W* is the weight loss in milligrams (mg), *A* the coupon surface area in cm² and *t* the immersion time in hours.

III.2 Effect of concentration of ACBP on the inhibition efficiency in 0.5M H₂SO₄.

The values of the corrosion rate obtained from weight loss measurements for different concentrations of inhibitor in 0.5 M H₂SO₄ are given in Table 2. It is found that ACBP inhibits the corrosion of mild steel in the acid at all concentration from 0.001 to 0.01 M. The effect of temperature on inhibitor performance was studied in 0.5 M H₂SO₄ between 25-45°C. Figure 2 shows the effect of temperature at different concentration of ACBP. It was observed that increase of temperature increase the corrosion rate. It is evident an interesting observation of the investigation is that ACBP gives excellent inhibitive performance in the acid solutions. The good inhibitive performance in acid solutions may be attributed to the presence of oxygen as well as sulphur atoms and double bonds in the same molecule. Nitrogen and sulphur containing compounds often provide excellent corrosion protection of metals.

The figure 3 shows clearly, that the inhibition efficiency of ACBP increases with increase in inhibitor concentration suggests that some of the molecules of ACBP are adsorbed on the metal surface thereby protecting the surface from further corrode attack. However inhibition decreases with increase in temperature. The maximum inhibition efficiency is lower at 25 °C than at 45 °C. This is in agreement with what is known about the dependence of adsorption on temperature that as temperature rises.

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Table 2: calculated values of corrosion rate for mild steel corrosion in 0.5M H₂SO₄ for different concentrations of ACBP at 25-45°C

ACBP(M)	NaCl(M)	W(g.cm ⁻² .h ⁻¹)		
		25°C	35°C	45°C
blank	-	0,0066	0,0084	0,0253
-	0,02	0,0039	0,0091	0,0133
0,001	0	0,0048	0,0063	0,0134
0,002	0	0,0040	0,0061	0,0119
0,003	0	0,0038	0,0061	0,0117
0,004	0	0,0040	0,0048	0,0097
0,005	0	0,0036	0,0041	0,0084
0,010	0	0,0009	0,0016	0,0068
0,001	0,02	0,0007	0,0014	0,0117
0,002	0,02	0,0007	0,0014	0,0117
0,003	0,02	0,0007	0,0013	0,0102
0,004	0,02	0,0006	0,0012	0,0095
0,005	0,02	0,0005	0,0009	0,0084
0,010	0,02	0,0004	0,0006	0,0067

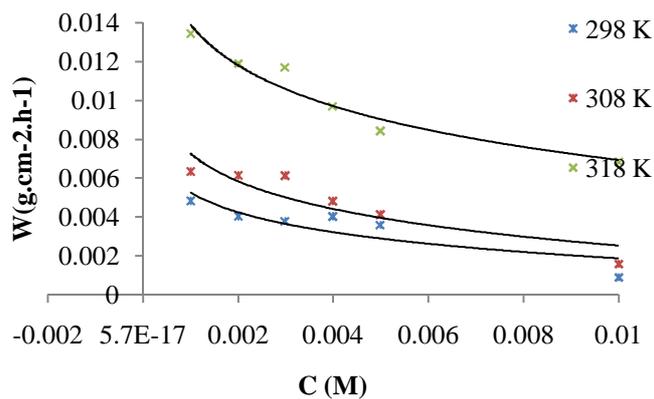


Figure 2. Plot of corrosion rate against ACBP concentration for mild steel corrosion in 0.5 M H₂SO₄ at different temperatures

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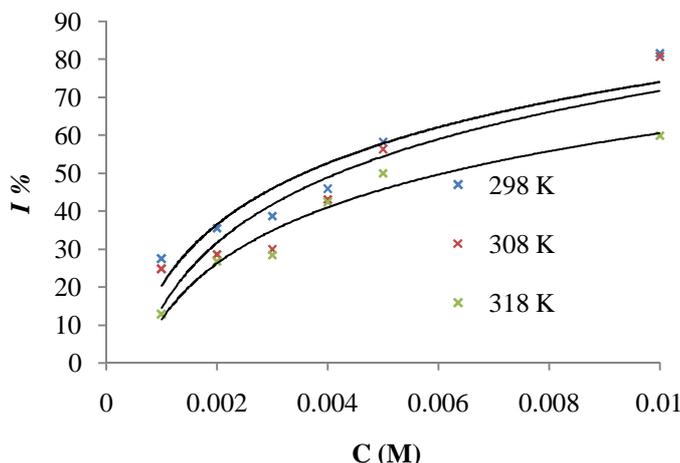


Figure 3. Plot of Inhibition efficiency against ACBP concentration for mild steel corrosion in 0.5 M H₂SO₄ at different temperatures

III.3 Inhibition efficiency obtained for different concentrations of ACBP with the addition of 0.02M NaCl at different temperatures

It has been observed that in the presence of a concentration of 0.02 M chloride in a 0.5M sulfuric acid solution, the efficiency is approximately 88 %, which proves a very good adsorbability on the carbon-steel's surface. It can be seen from the Table 3 and Figure 3 that inhibition efficiency rapidly increases with an increase in concentration of ACBP at the same temperature. At the same concentration of ACBP, however, inhibition efficiency decreases with increasing experimental temperature. The rise in temperature results in the increase in conductance of the aqueous acid medium and thereby increases the diffusion rate of hydrogen ions to the composite surface and hence the corrosion progresses faster at higher temperatures. The increase in *I* % may be due to the blocking effect of the surface by both adsorption

Table 3 .Inhibition efficiency for different concentrations of Acétyloxobenzopyranone without and with the addition of 0.02 M NaCl in 0.5 M H₂SO₄ at different temperatures

ACBP(M)	NaCl(M)	inhibition efficiency <i>I</i> %		
		25°C	35°C	45°C
blank	-	-	-	-
-	0,02	50,70	36,80	32,70
0,001	0	27,30	24,60	12,70
0,002	0	35,50	28,60	26,80
0,003	0	38,70	29,70	28,40
0,004	0	45,70	43,10	42,10
0,005	0	58,00	56,10	50,00
0,010	0	81,60	80,50	60,00
0,001	0,02	57,00	59,30	53,80
0,002	0,02	60,00	60,80	53,90
0,003	0,02	67,70	63,00	59,80
0,004	0,02	82,90	65,90	62,40
0,005	0,02	84,10	75,50	66,90
0,010	0,02	88,30	84,30	73,70

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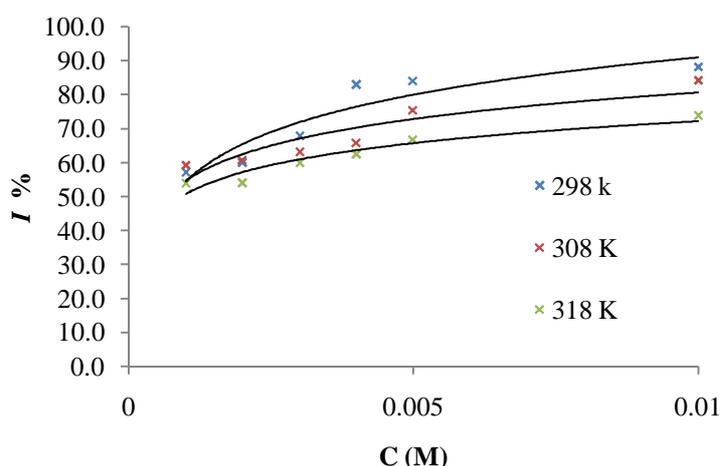


Figure 4: Inhibition efficiency for different concentrations of ACBP with the addition of 0.02M NaCl in 0.5M H₂SO₄ at different temperatures.

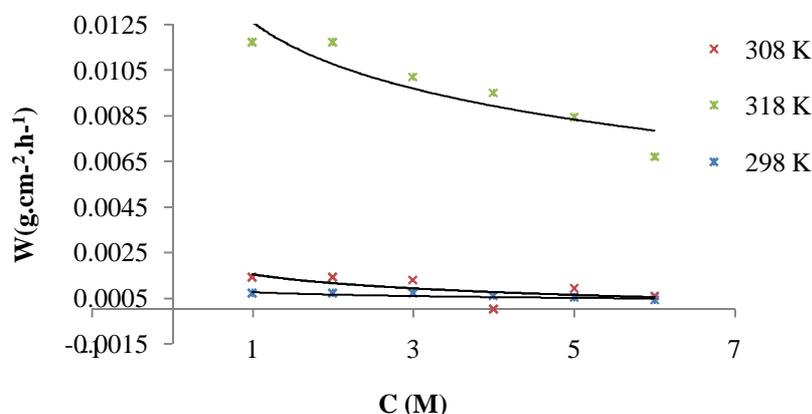


Figure 5. Corrosion rate for different concentrations of ACBP with the addition of 0.02M NaCl in 0.5M H₂SO₄ at different temperatures

and film formation mechanism which decreases the effective area of attack. Further reduction in corrosion rate observed on addition of 0.02 M NaCl to ACBP. The reduction in corrosion rate of ACBP when combined with chloride ions was found to be concentration dependent (table 3). The inhibition compared to the free acid solution efficiency is found to increase with increasing concentration of ACBP. The values of the inhibition efficiency $I \%$ decreases with rising the temperature, the highest protection efficiency of Acetyloxobenzopyranone combined with chloride was attained at 25°C. As per Ostovar 's explanation, the decrease in the inhibition efficiency of the inhibitor with increase in temperature might be due to adsorption and desorption of inhibitor. Adsorption and desorption of inhibitor molecules continuously occurs at the metal surface and an equilibrium exists between these two processes at a particular temperature [24].

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IV. ADSORPTION STUDIES

It is generally accepted that organic molecules inhibit corrosion by adsorption at the metal/solution interface and that the adsorption process is influenced by organic compounds chemical structures: the charge distribution in molecule [25], the chemical composition of solutions, the temperature and the electrochemical potential at the metal/solution interface. Adsorption isotherms provide information about the interaction among the adsorbed molecules themselves as well as their interaction with the electrode surface. The adsorption isotherm provides insight into the mechanism of corrosion inhibition. This is determined empirically by plotting the surface area of coverage Θ as a function of the concentration of the inhibitor. The isotherm gives the relationship between the coverage of an interface with the adsorbed species and the concentration of species in solution. The most frequently used adsorption isotherms are Langmuir, Frumkin, Temkin, Freundlich and the Flory-Huggins, Hill de Boer, Parsons, El-Awady and Bockris-Swinkels' isotherms. All of these isotherms are of the general form [26-31],

$$f(\Theta, x) \exp(-a\Theta) = K_{ads}C \quad (4)$$

Where $f(\Theta, x)$ is the configuration factor whose functional form depends on the physical model adopted and assumptions made in deriving the isotherm Θ is the degree of surface coverage, x is known as the size ratio which gives the number of water molecule replaced by the inhibitor molecule, a molecular interaction parameter whose value depends on the of molecular interactions in the adsorption layer and the degree of homogeneity of the surface, C is the inhibitor concentration and K_{ads} the equilibrium constant of adsorption process. Several adsorption isotherms were tested for fit with the experimental data. These include the Langmuir, Frumkin, Temkin, Freundlich and the El Awady isotherms. Among the isotherms mentioned above, the best description of the adsorption behavior of ACBP and ACBP + KI on mild steel specimens in 0.5M H_2SO_4 was Langmuir and Temkin adsorption isotherms, respectively. These models are expressed and presented in Equation 5 and 6 :

Langmuir adsorption isotherm:

$$(C/\Theta) = C + 1/K_{ads} \quad (5)$$

A plot of $Cinh/\Theta$ with C gives a straight line indicating that the adsorption of ACBP on the mild steel surface obeys Langmuir's adsorption isotherm (Figure 6). The equilibrium constant of adsorption process K_{ads} is related to the standard Gibbs free energy of adsorption (ΔG_{ads}^0) by the relation [32]:

$$\Delta G_{ads}^0 = -RT \ln((1/C_{solvent}) \cdot K_{ads}) \quad (6)$$

where $C_{solvent}$ represents the molar concentration of the solvent (in case of water it is 55.5 mol/dm³); R = universal gas constant $R = 8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$; and T is the absolute temperature (K_{ads}). The value of K_{ads} was calculated from intercepts of straight lines C/Θ axis and the ΔG_{ads}^0 values were calculated using Eq. (6). The K_{ads} value obtained for the system ACBP + KI is $10.10^2 \text{ (g.cm}^{-2}.\text{h}^{-1})$ is positive is large, indicating that the inhibitor is strongly adsorbed on the mild steel surface in the presence of iodide ions. Mean while, the calculated

Table 4: Calculated values of degree of surface coverage for mild steel corrosion in 1N H_2SO_4 for different systems at 298-318°K.

ACBP (M)	NaCl (M)	θ		
		25°C	35°C	45°C
0,001	0,02	0,57	0,59	0,54
0,002	0,02	0,60	0,61	0,54
0,003	0,02	0,68	0,63	0,60
0,004	0,02	0,83	0,66	0,62
0,005	0,02	0,84	0,75	0,67
0,010	0,02	0,88	0,88	0,74

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ΔG_{ads}^0 values is around -28.00 kJ. The negative values of ΔG_{ads}^0 indicate the spontaneous adsorption of the inhibitor on the mild steel mold steel surface. Generally, values of ΔG_{ads}^0 around -20 kJ. mol⁻¹ or lower are consistent with physisorption and those around -40 kJ. mol⁻¹ or higher involve chemisorption [33]. However, in the present case, the value of ΔG_{ads}^0 is found equal to -28.00 kJ mol⁻¹, which means that the adsorption of the combination of ACBP with NaCl on mild steel surface involves the physisorption [34].

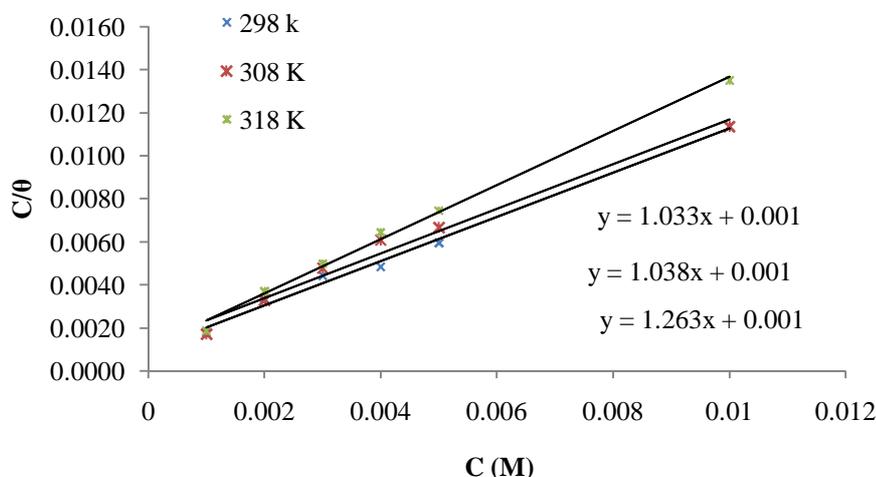


Figure 6: Langmuir adsorption isotherm for adsorption of ACBP on mild steel surface in 0.5M H₂SO₄ at 30°C.

Table 5: Adsorption equilibrium constant and standard free energy of adsorption of the investigated inhibitors for carbon mild steel in 1N H₂SO₄

T	K_{ads}	$-\Delta G^0$ (kJ.mol ⁻¹)	linear correlation coefficient
298	10 ³	27,10	0,993
308	10 ³	28,00	0,981
318	10 ³	28,90	0,994

Frumkin adsorption isotherm:

$$\text{Exp}(-f.\Theta) = C [1/55.5 (\text{exp}(-\Delta G_{ads}^0 / RT))] \quad (7)$$

Where Θ is the degree of surface coverage, f is the interaction term parameter (if $f > 0$, there is a lateral attraction, if $f < 0$, there is a lateral repulsion between the adsorbing molecules), c (in mg/L) is the inhibitor concentration, is the standard free energy of adsorption (kJ/mol). The Frumkin adsorption isotherm is a general expression since the limiting case for which $f = 0$ is representative of an interaction free behavior between adsorbed species and defines the Langmuir isotherm. Equation (7) can be rearranged to give Equation (8).

$$\text{Log } C = \text{log} (\Theta / 1 - \Theta) + A.\Theta + B \quad (8)$$

Where $A = -f/2.3$ and $B = (\Delta G_{ads}^0 / 2.3RT) + \text{log } 55.5$ and has the meaning of equilibrium constant of the adsorption process. A plot of $\text{Log } \Theta / (1 - \Theta)C$ against Θ gave almost a straight line (Fig. 7) which indicated that the inhibition

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action obeyed Frumkin with $R^2 = 0.992$. The positive value of f indicates that the adsorption of the tested compound is accompanied by mutual attraction of the inhibitor molecules [35-36].

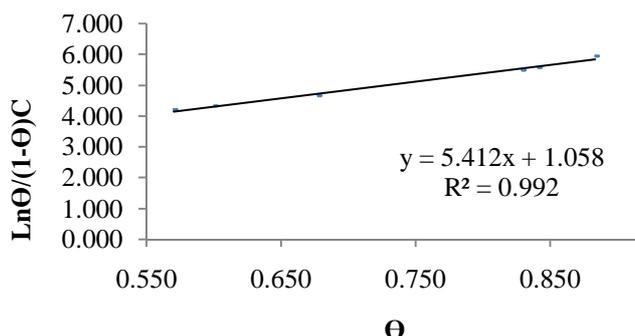


Figure 7: Frumkin adsorption isotherm for mild steel in 0.5M H_2SO_4 containing ACBP + NaCl at 30°C.

V. KINETIC/THERMODYNAMICS CONSIDERATIONS

Thermodynamic model is an important tool to study the mechanism of inhibitor on the corrosion of metal, a thermodynamic model for the adsorption process has been suggested. It has been known that efficient inhibitors should possess plentiful p-electrons and unshared electron pairs on either oxygen, nitrogen, sulfur or phosphorus atoms of the inhibitors to the d-orbitals of iron, and by means of transference of electrons chemical adsorption may occur on the steel surface [38-46]. Theoretical fitting of the corrosion data to the kinetic - thermodynamic model was tested to show the nature of adsorption. The apparent activation energy, E_a , for mild steel dissolution in 0.5M H_2SO_4 solution in the absence and presence of inhibitor (ACBP) and ACBP-halide mixtures was calculated from Arrhenius equation (47):

$$\log w_{corr} = \log A - \frac{E_a}{2.303RT} \quad (9)$$

The regression between $\log W_{corr}$ and $1/T$ was calculated by computer. Arrhenius plots of $\log W_{corr}$ vs. $1/T$ for the blank and different concentrations of the mixture gives straight lines with slopes of E_a/R are shown in Figure 8. All the parameters were calculated and given in Table 6. It is clear that the value of E_a in the presence of various ACBP concentrations + 0.02 M of NaCl are higher than that in the uninhibited acid solution. These results are according with the reported studies [48]. The increase of E_a in the presence of the inhibitor indicates that physical adsorption or weak chemical bonding between the mixture molecules and the steel surface might occur [49]. The activation energy rose with increasing inhibitor concentration, suggesting strong adsorption of inhibitor molecules at the metal surface. The increase in the activation energy was due to the corrosion reaction mechanism in which charge transfer was blocked by the adsorption of ACBP + NaCl molecules on the mild steel surface. It also revealed that the whole process was controlled by the surface reaction since the energy of the activation corrosion process in both the absence and presence of ACBP + NaCl was greater than 20 kJ mol^{-1} [50-51]. Higher E_a values in the presence of inhibitor compared to the blank solution indicates that the inhibitor will be effective at low temperatures, but efficiency will be considerably diminished at higher temperature [52]. In this study, such behavior was observed for the dependence of inhibition efficiency on temperature and further supports the proposed mechanism of physical adsorption.

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Table 6: Activation parameters for mild steel dissolution in 1N H₂SO₄ in the presence of mixture ACBP + NaCl

ACBP	A (g.m ⁻² .h ⁻¹)	E _a (kJ.mol ⁻¹)	linear correlation coefficient
Si	13,30.10 ⁵	144,50.10 ²	0,961
NaCl	49,55.10 ³	268,00.10 ²	0,921
0,001+NaCl	57,55.10 ¹⁴	899,00.10 ²	0,840
0,002+NaCl	11,80.10 ¹⁵	916,50.10 ²	0,910
0,003+NaC	13,20.10 ¹⁵	862,50.10 ²	0,901
0,004+NaCl	42,70.10 ¹⁵	891,50.10 ²	0,913
0,005+NaCl	85,10.10 ¹⁵	908,50.10 ²	0,886
0,010+NaCl	57,50.10 ¹⁵	899,00.10 ²	0,841

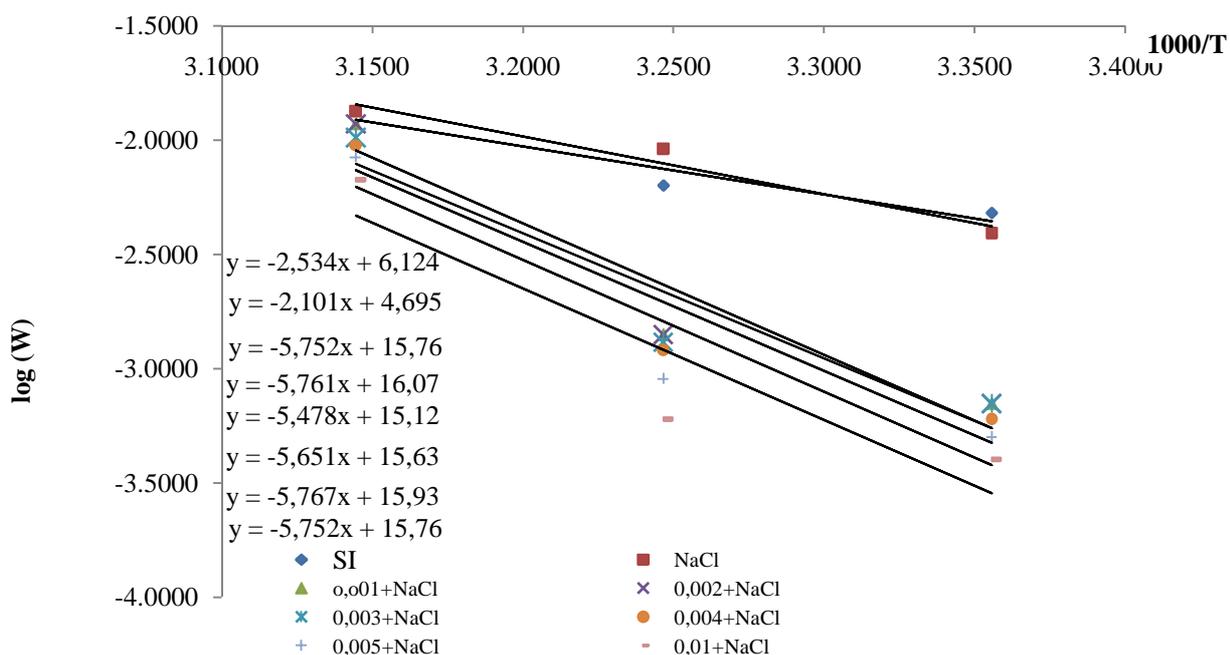


Figure 8: Arrhenius plot for carbon steel dissolution in the absence and presence investigated inhibitors

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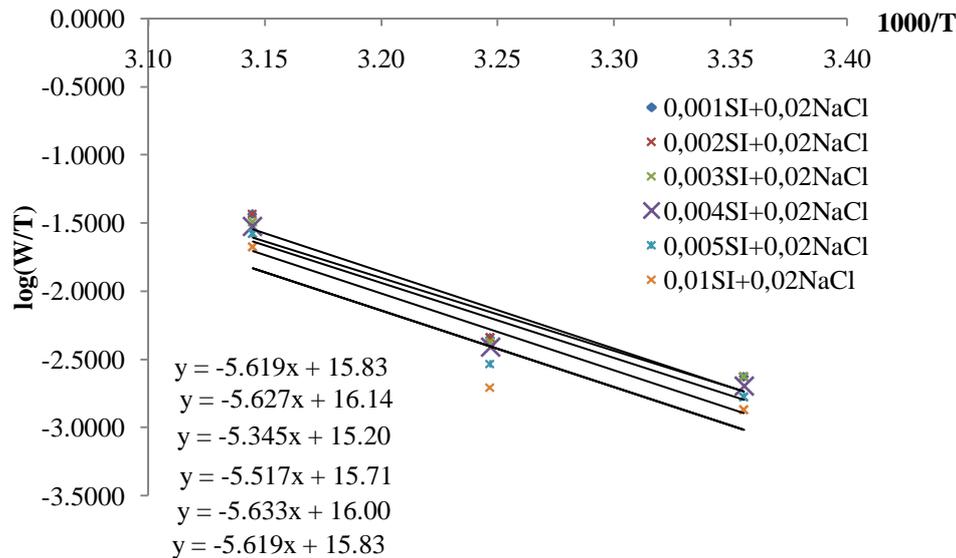


Figure 9: Transition state plot for carbon steel dissolution in the absence and presence investigated inhibitors

Table 7 explores thermodynamic parameters obtained from weight loss measurements of mild steel in 0.5M H₂SO₄ at 30°C for 6h. ΔG°_{ads} for ACBP + NaCl on mild steel showed negative indicate spontaneous adsorption of ACBP onto the mild steel surface [53] and strong interactions between inhibitor molecules and the metal surface.

$$\log \left(\frac{W_{corr}}{T} \right) = \left[\log \left(\frac{R}{hN} \right) + \frac{\Delta S^*}{2.303R} \right] - \frac{\Delta H^*}{2.303RT} \quad (10)$$

The values of the entropy of activation ΔS^* in the presence of the inhibitors are large and positive, indicate an endothermic adsorption nature, and the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorderness takes place during the course of transition from reactants to the activated complex [54]. The enthalpy of activation ΔH^* is another criterion on the basis of which the mode of adsorption can be explained. The positive values of ΔH^* show that the adsorption is endothermic with a

Table 7: Activation parameters of the dissolution reaction of mild in 1N H₂SO₄ in the presence of mixture ACBP + NaCl

SI	Ea	Ea - ΔH	ΔH^* (J.mol ⁻¹)	ΔS^* (J.mol ⁻¹ .k ⁻¹)
0,001	11,01	2.51	10.75	111,46
0,002	10,76	2.51	10.77	111,46
0,003	10,48	2.50	10,23	93,46
0,004	10,82	2.52	10,56	103,23
0,005	11.04	2.50	10,78	108,78
0,010	11.01	2.50	10,75	105,52

disordered phenomenon ascribed by the positive values of ΔS^* . In addition to this, the average difference in value of the $E_a - \Delta H^*_{ads}$ was found to be 2.51 kJ/mol, almost same as the value of RT (2.57 kJ/mol). This implies that the corrosion process of this metal in the acid medium is a unimolecular reaction.

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Synergism considerations

The extent of synergism existing between Acétyloxobenzopyranone and chloride ions can be analyzed by the synergism parameter (S) calculated using the relationship reported elsewhere [55-58] and given by:

$$S = \frac{(1-\theta_{1+2})}{(1-\theta_1-\theta_2)} \quad (9)$$

where $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$; θ_1 = surface coverage by chloride ions; θ_2 = surface coverage by cation Acétyloxobenzopyranone ; θ''_{1+2} = measured surface coverage by combined inhibitor (anion + cation). S approaches unity when there are no interactions between the inhibitor compounds, while $S > 1$ points to a synergistic effect; in the case of $S < 1$, the antagonistic interaction prevails.

Table 8: Synergism parameter (S_1) for different concentration of ACBP +0, 02 NaCl.]

ACBP (mM)	NaCl (M)	synergism parameter S	
		weight loss	efficiency
0,001	0,02	0,99	2,9
0,002	0,02	0,99	2,9
0,003	0,02	0,99	10,9
0,004	0,02	0,99	6,2
0,005	0,02	0,99	5,8
0,01	0,02	1,00	5,8

The values of the synergism parameter for the various concentrations of Acétyloxobenzopyranone studied from the gravimetric analysis are presented in Table 8. All values shown in this table are greater than unity. This is an indication that the enhanced inhibition efficiency resulting from the addition of chloride ions to Acétyloxobenzopyranone is synergistic in nature [59]. The strong chemisorption of chloride ions on the metal surface is responsible for the synergistic effect of chloride ions, in combination with ACBP + cation, the cations of the inhibitors are absorbed by coulombic attraction on the metal surface where chloride ions are already adsorbed. Stabilization of adsorbed chloride ions with ACBP + leads to greater surface coverage and thereby greater inhibition. The synergistic effect is due to the co-adsorption of halide ions on the surface which forms oriented dipoles with their negative ends toward the solution, thus increasing adsorption of organic molecules [60]. The increase in inhibition efficiency and synergism factor show that the mechanism of synergistic action is due to the coadsorption of molecules ACBP and chloride ions. This is very similar to the observation made by El-Warraky et al [61] for the adsorption synergistic of iodide ions with the benzotriazole or thiourea and iodide ion on the corrosion of Al-bronze in acidified 4% NaCl, it is found that in the presence of halide ions, the adsorbed halide ions make the iron surface into a negatively charged one and due to electrostatic interaction, strong adsorption of the cations of the inhibitors with halide covered surface takes place. The stabilization of adsorbed halide ions by means of electrostatic interaction with inhibitor cations leads to more surface coverage and hence greater inhibition.

VI. CONCLUSIONS

1. 3-Acétyl-4-oxo-benzopyranone an effectively inhibits mild steel corrosion in sulphuric acid, the inhibition efficiency increases with inhibitor concentration at all temperatures studied and also increases with rise in temperature
2. The addition of chloride ions to ACBP enhanced the inhibition efficiency due to synergistic effect.
3. The adsorptive behavior may be approximated by Langmuir and Frumkin adsorption isotherms.
4. The negative values of the free energy of adsorption is an indication that the process was spontaneous.
5. The values of S (synergistic parameter) obtained from the method employed are greater than unity showing the corrosion inhibition brought about by ACBP in combination with halides is synergistic in nature.

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REFERENCES

- [1] H. Zarrok , A. Zarrouk , R. Salghi , B. Hammouti , N. Chahboun, D. Ben Hmamou , R. Hmamouchi, T. Lakhlifi , A. Rochdi, A. El Assyry , "Inhibition of Carbon Steel Corrosion in HCl Media by Lipid Oil Melia", *Mor. J. Chem.* 2 N°1, pp. 10 -21, 2014.
- [2] M. El Achouri, S. Kertit, M. Salem, E.M. Essassi, M. Jellal, "3-Mercapto-1,2,4-Triazole derivatives as corrosion inhibitors for iron in hydrochloric acid solution", *Bull. Electrochem.*, Vol. 14 No.12, pp.462–8.23. 1998.
- [3] Lebe A. Nnanna, Kings O. Uchendu, Francis O. Nwosu, Uche Ihekoronye, Eti P. Eti , " Gmelina Arborea Bark Extracts as a Corrosion Inhibitor for Mild Steel in an Acidic Environment, *International Journal of Materials and Chemistry*, pp. 34-39, 4(2) 2014.
- [4] A. El bribri, M. Tabyaoui, H. El Attari, K. Boumhara, M. Siniti, B. Tabyaoui," Temperature effects on the corrosion inhibition of carbon steel in HCl (1M) solution by methanolic extract of Euphorbia Falcata.L", *J. Mater. Environ. Sci.* 2 (2) ,pp. 156-165, 2011.
- [5] M. Elachouri, M.S. Hajji, M. Salem, S. Kertit, J. Aride, R. Coudert, E. Essassi, "Some Nonionic Surfactants as Inhibitors of the Corrosion of Iron in Acid Chloride Solutions ", *Corrosion* 52, pp. 103-108, 1996.
- [6] Archana Gupta and M.M. Singh, "Inhibition of mild steel corrosion in formic acid by Thiourea, 2-Amino [4-p-Chloro Phenyl] Thiazole and different derivatives of their condensation products", *Port. Electrochem. Acta.* 17, pp. 21-43, 1999 .
- [7] M. M. Osman, A.M.A. Omar, A.M. Sabagh," Corrosion inhibition of benzyl triethanol ammonium chloride and its ethoxylate on steel in sulphuric acid solution", *Materials Chemistry and Physics* 50 , pp. 271-274, 1997.
- [8] Swati Yadav, Arpita Sharma, Guddi Choudhary, Alka Sharma, "Inhibitive and Adsorption Properties of Ethanolic Extract of Fruit of Azadirachta Indica on the Corrosion of Copper in HCl", *Vol. 3, Issue 9, IJIRSET*, pp. 26127-16137, 2014.
- [9] Hassan El attari, khadija Lahmadi and Mostapha Siniti, Adsorption and Inhibitive Properties of Tetradecyltriméthylammonium Chloride for the Corrosion of Carbon Steel in Acid Sulfuric, *International Journal of Latest Trends in Engineering and Technology (IJLTET)*. Vol. 6 Issue 2, pp. 423-434, 2015.
- [10] S.A. Ali, A.M. El-Shareef, R.F. Al-Ghamdi, M.T. Saeed, "The isoxazolidines: the effects of steric factor and hydrophobic chain length on the corrosion inhibition of mild steel in acidic medium", *Corros. Sci.*, 47, pp. 2659-2678, 2005.
- [11] Ehteram A. Noor," Temperature Effects on the Corrosion Inhibition of Mild Steel in Acidic Solutions by Aqueous Extract of Fenugreek Leaves", *Int. J. Electrochem. Sci.*, 2, pp. 996 – 1017, 2011.
- [12]S.A. Umoren, E.E. Ebenso, "the synergistic effect of polyacrylamide and iodide ions on the corrosion inhibition of mild steel in H₂SO₄" *Mater. Chem. Phys.* 106, pp. 387-399, 2007.
- [13] L. Larabi, Y. Harek, M. Traisnel, A. Mansri, "Inhibition behavior of mild steel in 1 M HCl in the presence of poly(4-vinylpyridine) (P4VP) and potassium iodide", *J. Appl. Electrochem.* 34, pp. 833-839, 2004
- [14] S.A. Umoren, O. Ogbobe, E.E. Ebenso, *Bull. Electrochem.* 22, pp. 155-157, 2006.
- [15] G.N. Mu, X.M. Li, G.H. Liu, *Corros. Sci.* 47, pp. 1932-1952, 2005.
- [16] E.E. Ebenso, H. Alemu, S. A. Umoren, I. B. Obot, Inhibition of mild steel corrosion in sulphuric acid using alizarin GG dye and synergistic iodide additive. *International Journal of Electrochemical Science* 3, pp.1325- 1339, 2008.
- [17] E. E. Ebenso, Effect of halide ions on the corrosion inhibition of mild steel in H₂SO₄ using methyl red. Part1. *Bulletin of Electrochem.*, 19(5), pp.209-216, 2004.
- [18] P. C. Okafor and Y. Zheng, "Synergistic inhibition behavior of methylbenzyl quaternary imidazoline derivative and iodide ions on mild steel in H₂SO₄ solutions," *Corrosion Science*, vol. 51, no. 4, pp. 850–859, 2009.
- [19] E. E. Ebenso, H. Alemu, S. A. Umoren, and I. B. Obot, "Inhibition of mild steel corrosion in sulphuric acid using alizarin yellow GG dye and synergistic Iodide Additive," *International Journal of Electrochemical Science*, vol. 3, pp. 1325–1339, 2008.
- [20] C. Jeyaprabha, S. Sathiyarayanan, S. Muralidharan, and G. Venkatachari, "Corrosion inhibition of iron in 0.5mol L⁻¹ H₂SO₄ by halide ions," *Journal of the Brazilian Chemical Society*, vol. 17, no. 1, pp. 61–67, 2006
- [21] X. Li, S. Deng, and H. Fu, "Synergistic inhibition effect of 6-benzylaminopurine and iodide ion on the corrosion of cold rolled steel in H₃PO₄ solution," *Corrosion Science*, vol. 53, no. 11, pp. 3704–3711, 2011.
- [22] K. C. Emregul and O. Atakol, "Corrosion inhibition of iron in 1 M HCl solution with Schiff base compounds and derivatives," *Materials Chemistry and Physics*, vol. 83, no. 2-3, pp. 373–379, 2004.
- [23] K. Orubite-Okorosaye, N. C. Oforka, Corrosion Inhibition of Zinc on HCl using Nypa fruticans Wurmb Extract and 1,5 Diphenyl Carbazone, *J. Appl. Sci. Environ. Mgt.* 8 , pp. 57–61, 2004.
- [24]A. Ostovari, S. M. Hoseinieh, M. Peikari, and S. R. Shadizadeh, Corrosion inhibition of mild steel in 1 M HCl solution by henna extract and Tannic acid, *Corrosion Science*, vol. 51, no. 9, pp. 1935–1949, 2009.
- [25] MA. Ameer , E. Khamis , G. Al-Sanani "Adsorption studies of the effect of thiosemicarbazides on the corrosion of steel in phosphoric acid" *Adsorpt. Sci. Tech.*, 18, pp. 177-194, 2000.
- [26] M. Iannuzzi , GS. Frankel, "Mechanisms of corrosion inhibition of AA2024-T3 by vanadates" *Corros. Sci.*, 49: pp. 2371-2391, 2007.
- [27] EE. Ebenso, NO. Eddy, AO. Odiongenyi, "Corrosion inhibition and adsorption properties of methacarbamol on mild steel in acidic medium" *Portugaliae Electrochemica Acta.*, 27(1), pp. 13-22, 2009.
- [28] S. A. Umoren, "Inhibition of aluminium and mild steel corrosion in acidic medium using gum arabic. Cellulose "15, pp. 751- 761, 2008.
- [29] I. B. Obot, N. O. Obi-Egbedi, "Ipomoea involcrata as an ecofriendly inhibitor for aluminium in alkaline Medium", *.Portugaliae Electrochimica Acta* 27, pp.517- 229, 2009.
- [30] M. Bouklah, N. Benchat, B. Hammouti, A. Aouniti, S. Kertit, Thermodynamic characterisation of steel corrosion and inhibitor adsorption of pyridazine compounds in 0.5 M H₂SO₄, *Materials Letters*, 60 , pp. 1901- 1905, 2006.
- [31] H. Ashassi-Sorkhabi, B. Shaabani, and D. Seifzadeh, "Effect of some pyrimidinic Schiff bases on the corrosion of mild steel in hydrochloric acid solution," *Electrochimica Acta*, vol. 50, no. 16- 17, pp. 3446–3452, 2005.
- [32] S. Martinez, "Inhibitory mechanism of mimosa tannin using molecular modeling and substitutional adsorption isotherms." *Mater. Chem. Phys.*, 77, pp. 97-102, 2002.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 5, Issue 2, February 2016

- [33] Emregul KC, Hayvali M "Studies on the effect of vanillin and protocatechualdehyde on the corrosion of steel in hydrochloric acid" *Mater.chem. Phys.*, 83, pp. 209-216, 2004.
- [34] M. Donahue and K. Nobe, "Theory of Organic Corrosion Inhibitors: Adsorption and Linear Free Energy Relationships" *J. Electrochem. Soc.* 112, pp. 886-891, 1965.
- [35] M. Christov, A. Popova, "Adsorption characteristics of corrosion inhibitors from rate measurements", *Corros. Sci.* 46, pp. 1613-1630, 2004.
- [36] J. Aljourani, K. Raeissi, M. A. Golozar, "Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1 M HCl solution", *Corros. Sci.* 51, pp. 1836-1843, 2009.
- [37] Y. Feng, K.S. Siow, W.K. Teo, A.K. Hsieh, "The synergistic effects of propargyl alcohol and potassium iodide on the inhibition of mild steel in 0.5 M sulfuric acid solution", *Corros. Sci.* 41, pp. 709-729, 1999.
- [38] X.H. To, N. Pebere, N. Pelaprat, B. Boutevin, Y. Hervaud, "A corrosion-protective film formed on a carbon steel by an organic phosphonate", *Corros. Sci.* 39, pp. 1925-1934, 1997.
- [39] L.B. Tang, G.N. Mu, G.H. Liu, "The effect of neutral red on the corrosion inhibition of cold rolled steel in 1.0 M hydrochloric acid" *Corros. Sci.* 45, pp. 2251-2262, 2003.
- [40] M.A. Quraishi, H.K. Sharma, 4-Amino-3-butyl-5-mercapto-1,2,4-triazole: a new corrosion inhibitor for mild steel in sulphuric acid, *Mater. Chem. Phys.* 78, pp. 18-21, 2002.
- [41] H. El Attari, A. El Bribri, L. Mhaidra, F. Bentiss and M. Siniti, "Synthesis and Anticorrosion for Carbon Steel Of 4-Amino-3,5 Bis (4-Hydroxy-3-Methoxy)-1,2,4-Triazole in Hydrochloric Acid Solution", *American Journal of Engineering Research*, Volume-4, Issue-3, pp. 44-51, 2015.
- [42] E. E. Ebenso, P. C. Okafor, O. E. Offiong, B. I. Ita, U. J. Ibok, and U. J. Ekpe, "Comparative investigation into the kinetics of corrosion inhibition of aluminium alloy AA 1060 in acidic medium," *Bulletin of Electrochemistry*, vol. 17, no. 10, pp. 459-464, 2001.
- [43] M. A. Ameer, E. Ehamis and G. Al-Senani "Adsorption studies of the effect of thiosemicarbazides on the corrosion of steel in phosphoric acid", *Adsorption Sci. Technol.*, Vol.18, pp. 177-194, 2000.
- [44] Ashish Kumar Singh, Sudhish Kumar Shukla, Manjeet Singh and Quraishi. M.A "Inhibitive effect of ceftazidime on corrosion of mild steel in hydrochloric acid solution", *Mater. Chem. Phys.*, Vol.129, pp. 68-76, 2011.
- [45] G. Banerjee and S.N. Malhotra "Contribution to adsorption of aromatic amines on mild steel surface from HCl solutions by impedance, UV, and Raman spectroscopy", *Corrosion*, Vol.48, pp. 10-15, 1992.
- [46] A. Bellaouchou, B. Kabkab, A. Guenbour, and A. Ben Bachir "Corrosion inhibition under heat of 904L stainless steel in phosphoric acid by benzotriazole", *Prog. Org. Coat.*, Vol.41, pp. 121-127, 2001.
- [47] N.O. Eddy and S.A. Odoemelam, Inhibition of corrosion of mild steel in acidic medium using ethanol extract of Aloe vera Pigment & Resin *Technology* 38/2, pp. 111-115, 2009.
- [48] S. Acharya, S. and S. N. Upadhyay, "The inhibition of corrosion of mild steel by some fluoroquinolones in sodium chloride solution", *Trans. Indian Inst. Met.*, Vol. 57 No. 3, pp. 297-306, 2004.
- [49] K. C. Emregul, A. A. Akay and O. Atakol, "The corrosion inhibition of steel with Schiff base compounds in 2M HCl", *Materials Chemistry & Physics*, Vol. 93 No. 1, pp. 325-9, 2005.
- [50] H. Ashassi-Sorkhabi, Z. Ghasemi and D. Seifzadeh, "The inhibition effect of some amino acids towards the corrosion of aluminum in 1M HCl solution", *Applied Surface Science* I, Vol. 29 No. 3, pp. 408-18, 2005.
- [51] D. S. Sheatty, P. Shetty and H. V. S. Nayak, "Inhibition of mild steel corrosion in acidic medium by N-(2-thiophenyl) N-phenyl thiourea", *Journal of Chilean Chemical Society*, Vol. 51 No. 2, pp. 849-53, 2006.
- [52] A. A. Khadom, A. S. Yaro, A. S. Al-Taie, A. A. H. Kadum, "Electrochemical, Activations and Adsorption Studies for the Corrosion Inhibition of Low Carbon Steel in Acidic Media", *Port. Electrochem. Acta.*, 27(6), pp. 699-712, 2009
- [53] H. El Attari, K. Lahmadi, A. El bribri, M. Siniti, "The Adsorption and Corrosion Inhibition of Non-Ionic Surfactant on Carbon Steel Surface in Hydrochloric Acid, International", *Journal of Materials and Chemistry* 5(3), pp.77-83, 2015
- [54] Kazaure Z. Sulay, Agbogo U. Victor, Bognet Obed, Adeyemi O. Olufemi, "Kinetics and Thermodynamic Study of Inhibition Potentials by Ethoxyethane Extracts of *Cochlospermum tinctorium* for the Oxoacid Corrosion of Mild Steel", *International Journal of Materials and Chemistry*, 5(3) pp. 64-76, 2015.
- [55] A. El bribri, H. El attari, M Siniti and M. Tabyaoui, "Temperature effects on the corrosion inhibition of carbon steel in 1N H₃PO₄ solution by methanolic extract of *Euphorbia falcata* L.", *Mor. J. Chem.* 3 N^o2, pp. 286-297, 2015.
- [56] M. Bouklah, A. Attayibat, S. Kertit, A. Ramdani and B. Hammouti "A pyrazine derivative as corrosion inhibitor for steel in sulphuric acid solution", *Appl. Surf. Sci.*, Vol. 242, pp. 399-406, 2005.
- [57] F. El-Hajjaji, R.A. Belkhamima, B. Zerga, M. Sfaira, M. Taleb, M. Ebn Touhami, B. Hammouti, S.S. Al-Deyab and Eno Ebenso, "Temperature Performance of a Thione Quinoxaline Compound as Mild Steel Corrosion Inhibitor in Hydrochloric Acid Medium" *Int. J. Electrochem. Sci.*, 9, pp. 4721 - 4731, 2014.
- [58] T. Grchev, M. Cvetkovska, J.W. Schultze, "the electrochemical testing of polyacrylic acid and its derivatives as inhibitors of corrosion", *Corros. Sci.* 32, pp. 103-112, 1991.
- [59] D. Zhang, X. He, Q. Cai, L. Gao, G. Kim, Arginine self-assembled monolayers against copper corrosion and synergistic effect of iodide ion, *J. Appl. Electrochem.* vol., Issue 8, pp. 1193-1198, 2009.
- [60] Loutfy H Madkour, Amara M Hassanein, Mohamed M Ghoneim, Safwat A Eid, *Monatshefte für Chemie/Chemical Monthly*, vol. 132, Issue 2, pp. 245-258, 2001
- [61] S. S. Shivakumar and K. N. Mohana, Corrosion Inhibition Performance of Azure A on Mild Steel in Sulphuric Acid Medium, *Der Chemica Sinica*, 3(6), pp.1455-1467, 2012.