

Original Research Article

Inhibitive and Synergistic Properties of Ethanolic Extract of *Moringa oleifera* Leaves on the Corrosion of Zinc in HCl Solution

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Running title: Inhibitive Extract of corrosion

ABSTRACT

The potentials of ethanolic extract of *Moringa oleifera* leaves as corrosion inhibitor was investigated by evaluating the corrosion behaviour of Zinc immersed in 0.5M, 1.0M, 1.5M and 2.0M HCl (corroderent) solutions each containing varied concentration of the extract (0.1g/L, 0.3g/L and 0.5g/L) and halides (0.1M, 0.3M and 0.5M each of KCl and KI) for synergism using thermometric method. Maximum temperature attained, reaction time, synergism parameter and adsorption characterizations were utilized to evaluate the corrosion inhibition, synergism and adsorption properties of the extract. The results revealed that the corrosion of Zinc decreases with increase in concentration of ethanol extract and halides which are both inhibitors; also, it increases with increase in HCl (corroderent) concentration. The addition of KI and KCl to the extract, improve the values of inhibition efficiency of the extract in the order KI > KCl. In all cases, KI exhibits least effect on the corrosion of Zinc in comparison with KCl. Results obtained from adsorption studies indicated that, the ethanol extract, KCl and KI were adsorbed on the surface of the Zinc and that the adsorption fit excellently with the assumptions of the Langmuir adsorption isotherm model on the platform of Chemical Adsorption. All data acquired revealed that the ethanol extract is an efficient inhibitor of corrosion in acid medium due to its phytochemicals: saponins, tannins, flavonoids, glycosides, carbonhydrates, reducing sugars, terpenoids, steroids and alkaloids.

Key words: Adsorption, Corrosion Inhibitor, Halides, *Moringa oleifera*, Synergism

1. INTRODUCTION

Scientists are relentless in seeking better and more efficient ways of combating the corrosion of metals. Among other methods, adding inhibitors to the corrosion environment has been employed. The use of inhibitors has been well documented as an effective method of protecting metallic materials from corrosion [1]. Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. The efficiency of these inhibitors is sometimes improved by the addition of some other compounds which act in synergism. Inhibitors are added to many systems, namely, cooling systems, refinery units, chemicals, oil and gas production units, boiler, and so forth [1].

Most green inhibitors contain hetero atoms such as Oxygen (O), Nitrogen (N), and Sulphur (S) with multiple bonds in their molecules through which they are adsorbed on the metal surface. It has been observed that adsorption depends mainly on certain physicochemical properties of the inhibitor group, such as functional groups, electron density at the donor atom, π -orbital character, and the electronic structure of the molecule [2]. Many studies have been carried out using synergistic corrosion inhibitors [3-4].

Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and environment. The use of chemical inhibitors has been limited because of the environmental threat recently, due to environmental regulations. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system, namely, kidneys or liver, or disturbing a biochemical process or disturbing an enzyme system at some sites in the body. The toxicity may be manifested either during the synthesis of the compound or during its applications [2].

In the search for more environmentally friendly and readily available inhibitors, researchers have reported the use of local plants such as *Vernonia amygdalina* [5], *Lawsonia* [6]; among others. In line with these *Nypa fruticans' wurmba* local plant has also been reported as inhibitor for mild steel in HCl medium, which has similar inhibition properties with 1, 5-di-phenyl carbazone [7]. Effect of KI by extract of *Nypa Fruticans' wurmb* was studied and showed that the mild steel is more efficiently inhibited by *Nyapafruticans' wurmb* in presence of KI than pure extract of *Nyapafruticans' wurmb* [7-8]. The inhibitive and synergistic properties of

Ethanolic Extract of *Anogeissus leiocarpus* leaves on the corrosion of Aluminium in HCl solution was studied and showed that inhibition was greatest by the synergistic combination of extract and KI [9].

The objective of this work is to focus on the inhibitive properties of some natural products particularly *Moringa oleifera* leaves for use as corrosion inhibitors for zinc in acid medium. The choice of *Moringa oleifera* leaves is significant for it has some phytochemical properties, and there was no report in literature on the use of this plant on corrosion inhibitors.

2. MATERIALS AND METHODS

The elemental composition of zinc sheets used for this study was determined using a spark spectrometric analyzer and summarized in table 1.

Table 1. Elemental composition of Zinc sheets

Element	Weight (%)
Pb	0.001
Fe	0.002
Cd	0.001
Cu	0.003
Zn	99.993

These sheets were mechanically press-cut into 5 x 4 cm coupons of 0.11cm thickness. The coupons were screened carefully to check for rough edges, which could influence the corrosion monitoring process. Surface treatment of the coupons was carried out by degreasing in absolute ethanol and drying in acetone. They were then stored in moisture free desiccators before use. All reagents and chemicals used for the study were of Analar grade and double distilled water was used for their preparation.

2.1 Extraction of plant

Samples of *Moringa oleifera* leaves were obtained from Ganaja Village, Lokoja, after which they were identified and named at Biological Sciences Department, Federal University, Lokoja, Nigeria. The Samples were washed, air dried, ground, sieved and soaked in a solution of ethanol for 1 week to percolate and were filtered. The filtrates were further subjected to concentration using a rotary vapour (BUCHI R110, 40°C) to obtain thick syrup which was later allowed to air dry. The dry extract so obtained were used in preparing different concentrations of the plant extract by dissolving 0.1g, 0.3g and 0.5g of the extract each differently in 1 dm³ of 0.5, 1.0, 1.5 and 2.0 M HCl respectively [10].

2.2 Chemical analysis

The various methods for the identification and quantification of Phytochemicals in plant extract were used for the identification of the various phytochemicals in ethanol extract of *Moringa oleifera* leaves [10, 11-12].

2.3 Thermometric method

The reaction vessel is a three-necked round bottom flask. The procedure for determining the corrosion behaviour by this method was described elsewhere [9]. The flask was well lagged to prevent heat losses. In the thermometric method, the corrodent (HCl) concentration was varied at 0.5, 1, 1.5 and 2 M, while halides (KCl and KI) were used at varying concentrations of 0.1, 0.3 and 0.5M (for synergism). The volume of the test solution used was 50cm³. The initial temperature in all the experiments was kept at room temperature. The progress of the corrosion reaction was monitored by determining the changes in temperature with time (each minute for the first five minutes, each five minutes for the next 25 minutes and each ten minutes for the last thirty minutes) using a calibrated thermometer (0 - 100°C) to the nearest ± 0.05°C. The data was obtained for a period of one hour for each sample solution.

From the data obtained, Reaction number was calculated as follows: From the rise in temperature of the system per minute, the reaction number (RN) was calculated using equation (1):

$$RN(^{\circ}C/min) = \frac{T_m - T_i}{t} \quad (1)$$

Where T_m is the maximum temperature attained by the system, T_i is the initial temperature and t is the time required to reach the maximum temperature.

From the above, the inhibition efficiency (%IE) of the used inhibitor was computed using equation (2):

$$\%IE = \frac{RN_f - RN_i}{RN_f} \quad (2)$$

Where RN_f is the reaction number of aqueous acid in the absence of *Moringa oleifera*, and RN_i is the reaction number of aqueous acid in the presence of *Moringa oleifera* extract or the halide additives where applicable [9].

3. RESULTS AND DISCUSSION

The result of the inhibitive and synergistic properties of *Moringa oleifera* extract and halides on the corrosion of Zinc in HCl is presented as follows:

3.1 Effect of corrodent concentration only on the corrosion of Zinc coupon

Figure 1 presents the effect of reaction temperature variation with time for the corrosion of Zinc in varying HCl solutions was conducted. The temperature of the reaction system was observed to increase with increasing concentration of the corrodent, HCl. Corrosion rate increases with increasing temperature. The tendencies for partial desorption of inhibitor from the metal surface and the metal dissolution increases with temperature. Therefore, an increase in concentration of the corrodent increases the rate of corrosion of Zinc [13].

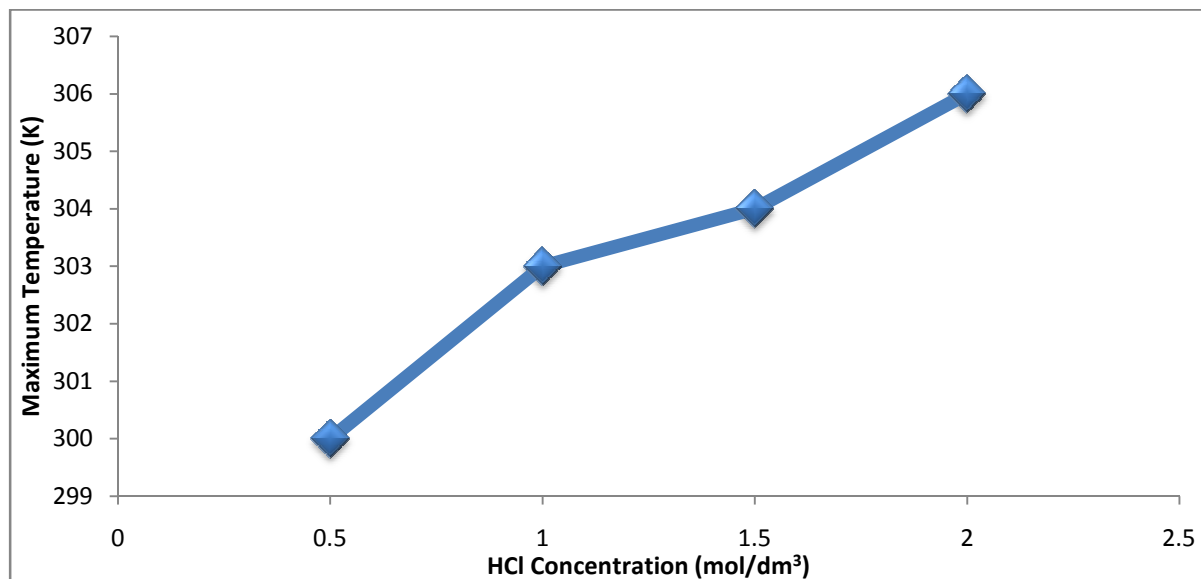


Figure 1. Variation of temperature with HCl concentration for the corrosion of Zinc

3.2 Effect of plant extract and corrodent on the corrosion of Zinc coupon

The result of the effect of plant extract in different HCl solutions on the corrosion of zinc coupons was also tested. Observation showed that the presence of the plant extracts reduces the reaction temperatures and also the rate of reaction, thereby inhibiting the corrosion of Zinc. It was also observed that the higher the concentration of the plant extract the better the inhibition while the higher the corrodent concentration the higher the rate of corrosion. This may be attributed to the increase in number of adsorption active centers at higher concentration of the inhibitor. Similar results have been reported earlier [9, 11-12, 14].

3.3 Effect of halide type and corrodent without plant extract on Zinc corrosion

Figures 2, 3 and 4 presents the corrosion of zinc coupons in 0.1M, 0.3M and 0.5M KCl and KI respectively in varying HCl solutions. It can be observed in all the systems that KI has the least corrosion effect on Zinc in the three corrodent concentrations tested. This could be attributed to the large ionic size of iodide ion and its low electronegativity when compared to chloride. Electronegativity decreases from Cl^- to I^- ($\text{Cl}^- = 3.0$, $\text{I}^- = 2.5$), while the atomic radius also increases from Cl^- to I^- ($\text{Cl}^- = 0.90\text{\AA}$, $\text{I}^- = 1.35\text{\AA}$) [9].

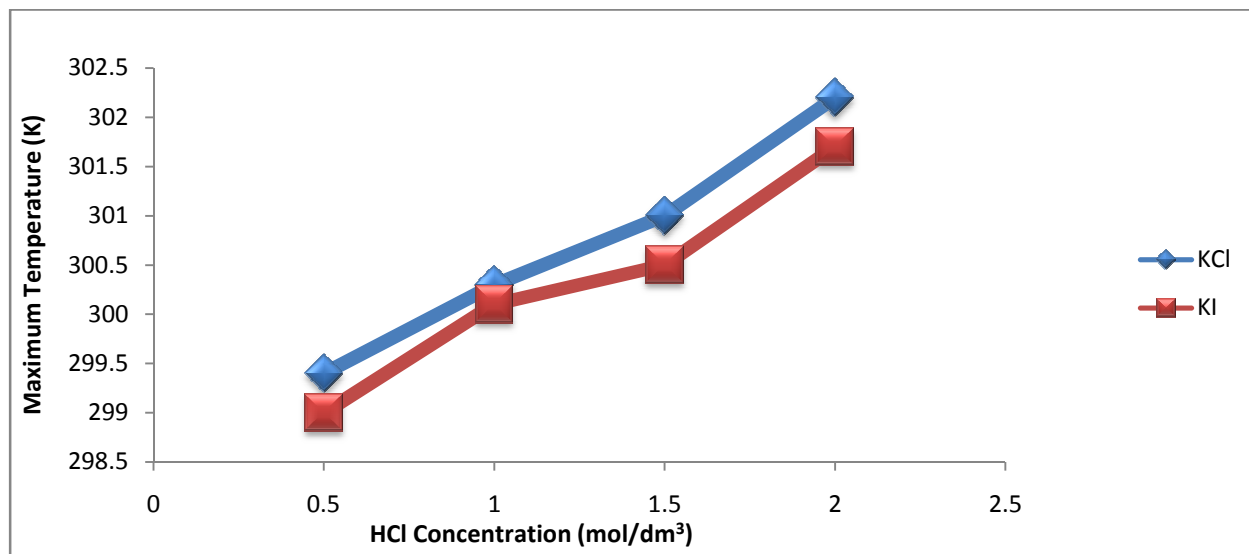


Figure 2. Variation of temperature with HCl concentration for the corrosion of zinc in 0.1M KCl and KI

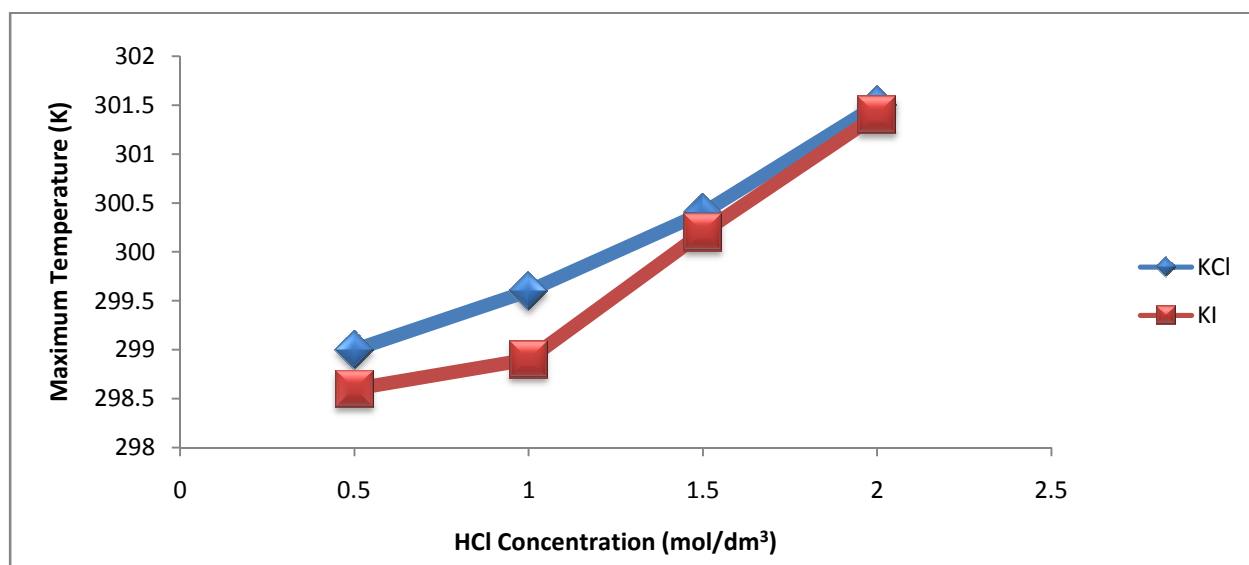


Figure 3. Variation of temperature with HCl concentration for the corrosion of zinc in 0.3M KCl and KI

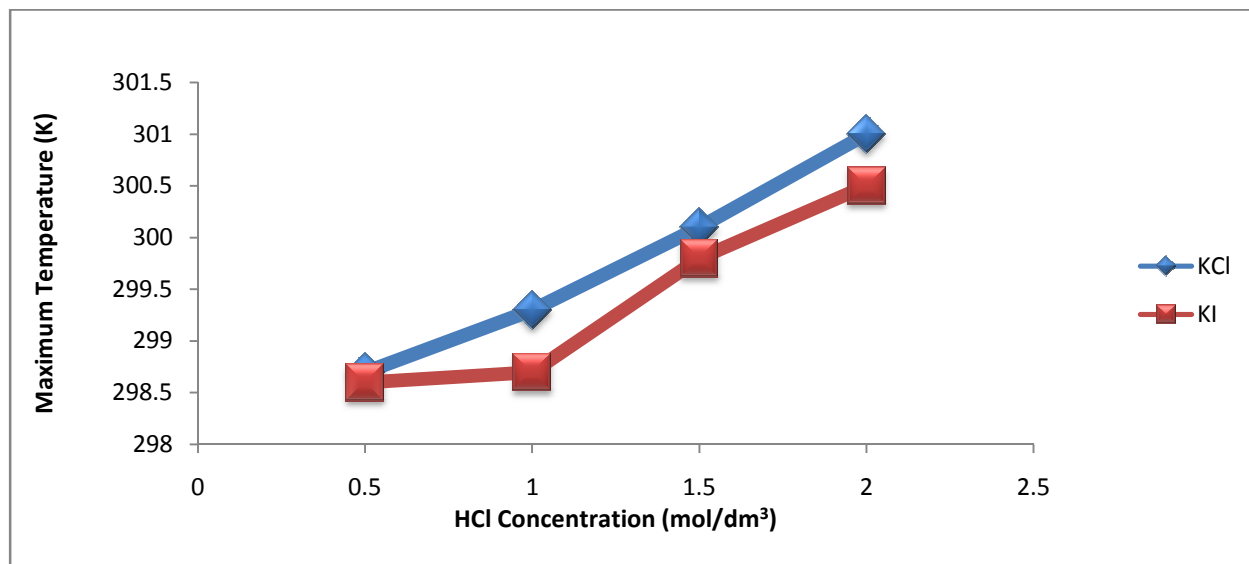


Figure 4. Variation of temperature with HCl concentration for the corrosion of zinc in 0.5M KCl and KI

3.4 Effect of halide type with plant extract on the corrosion of Zinc in HCl solution

The addition of plant extract (0.1g/L) to the corrosion solution containing HCl and the halides reduced considerably the reaction temperature thereby reducing the rate of corrosion. Comparing the inhibition efficiencies therefore, KI had the best inhibition property in the presence of the plant extract. This can again be attributed to the fact that Iodide has large ionic size and low electronegativity compared to chloride. Similar results were obtained when the concentration of the plant extract was increased to 0.3g/L and then to 0.5g/L. This is evident in Figures 5, 6 and 7 respectively showing the variation of temperature with time for the corrosion of Zinc coupon in 0.1, 0.3 and 0.5M KCl and KI. In all cases, the inhibition increases at 0.5 and 1.0M HCl solution with a rapid decrease in inhibition at 1.5M and 2.0M HCl solution. Since phytochemicals are oxygen, nitrogen or sulphur containing organic compounds with lone pairs of electrons, they may be protonated in strong acidic solutions leading to positive charge. Zinc surface is known to have positive charge, thus it is difficult for the positively charged phytochemical to approach the zinc surface at high acidic concentration due to electrostatic repulsion and perhaps explains why these compounds exhibit decreasing inhibition efficiencies at higher HCl concentration [15]. For the halides, reason may be attributed to competition between Chloride, Iodide and plant extract on the Zinc surface at higher HCl concentration. Similar results have been reported earlier [9].

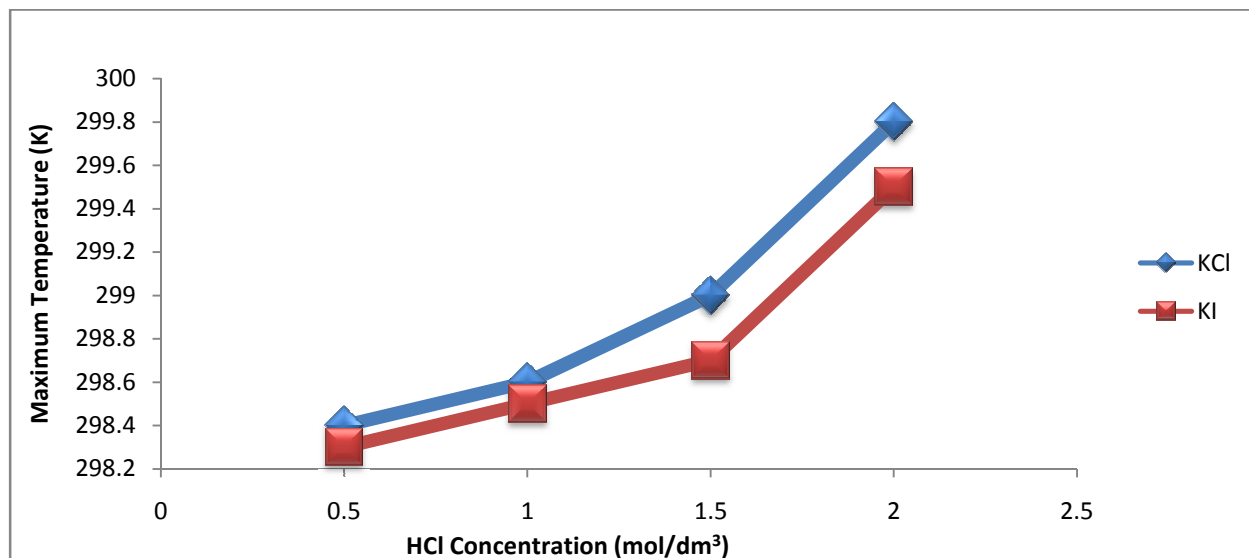


Figure 5. Variation of temperature with HCl concentration for the corrosion of zinc in 0.1M KCl and KI, and 0.3g/L inhibitor

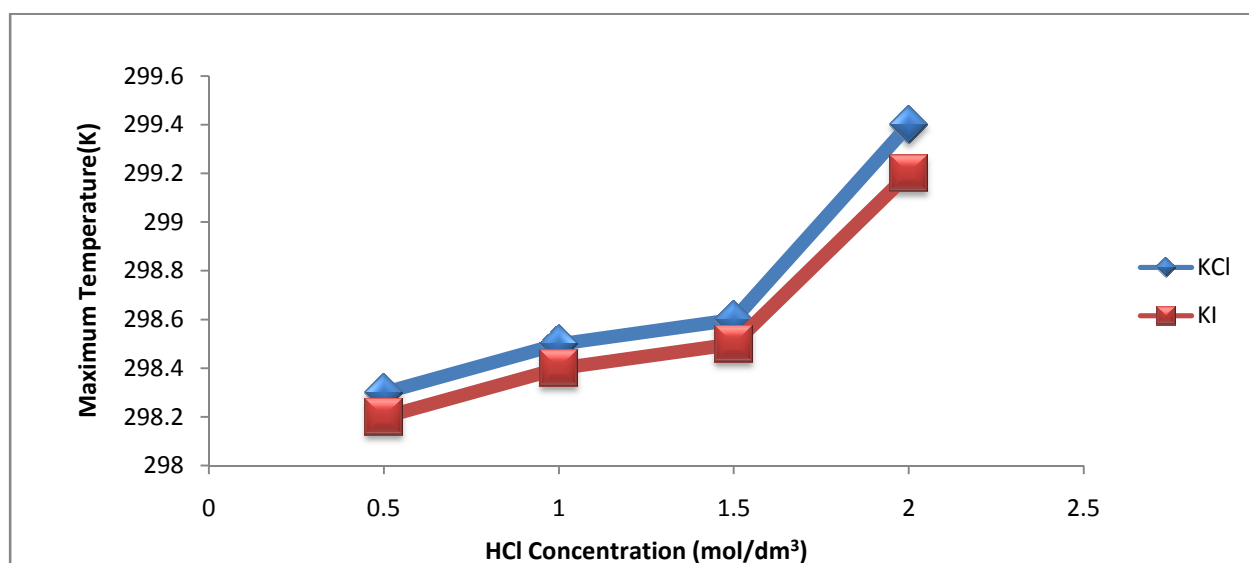


Figure 6. Variation of temperature with HCl concentration for the corrosion of zinc in 0.3M KCl and KI, and 0.3g/L inhibitor

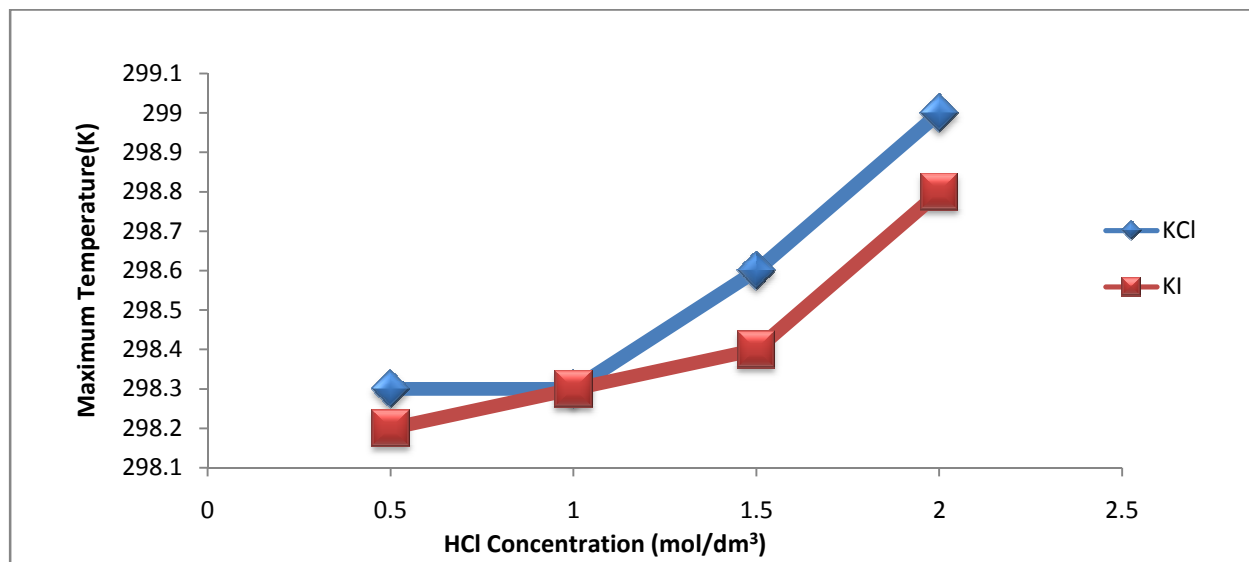


Figure 7. Variation of temperature with HCl concentration for the corrosion of zinc in 0.5M KCl and KI, and 0.3g/L inhibitor

Table 2 presents the various phytochemicals detected in the plant extract with regards to their concentration.

Table 2. Phytochemical composition of ethanol extracts of *Moringa oleifera* leaves.

Phytochemicals	Results
Flavonoids	++++
Carbohydrates	++
Alkaloids	++
Reducing Sugars	++
Steroids	++
Tannins	+
Saponins	+
Glycosides	+
Terpenoids	+

Resins	-
Proteins	-
Fats and Oil	-

189

190 Key: +++++ (High Concentration); ++ (Moderate); + (Low) ; - (Not detected)

191 It is therefore concluded that the inhibitive properties of Moringa oleifera is due to the presence
 192 of phytochemicals shown in table 2 above. Phytochemicals are Oxygen, Nitrogen or Sulphur
 193 containing organic compounds with presence of non shared electron pairs and p-electrons in
 194 triple or conjugated double bonds which are perhaps donated into available empty orbitals on the
 195 Zinc surface; hence they are expected to be good corrosion inhibitors [15].

196 3.5 Percentage inhibition efficiency

197 Table 3 and 4, presents the calculated values of inhibition efficiencies for the corrosion of
 198 Zinc in varying KCl, KI, plant extract and HCl concentrations. Table 3 shows the percentage
 199 inhibition efficiencies for the corrosion of Zinc in varying concentrations of KCl, Plant extract
 200 and HCl. Observation showed that as the concentration of the plant extract increases, the
 201 inhibition efficiencies also increase. Increase in the concentration of KCl also leads to an
 202 increase in corrosion inhibition.

203 **Similar results** from the corrosion inhibition efficiencies for the corrosion of Zinc in
 204 varying KI, plant extract and HCl concentrations **are shown** in table 4. The only observed
 205 difference is the higher inhibition efficiencies of KI in comparison with KCl, in which the reason
 206 was stated earlier. In all cases, the inhibition efficiencies decrease with increasing corrodent, HCl
 207 concentration. **Similar results have been reported elsewhere [13].**

208 **Table 3. Calculated values of inhibition efficiencies (%) for zinc corrosion in varying HCl,**
 209 **plant extract and KCl concentrations**

Corrodent Conc.		0.5M HCl			1M HCl			1.5M HCl			2M HCl		
KCl Conc.	Extract conc.	KCl +			KCl +			KCl +			KCl +		
		KCl	P.E	P.E	KCl	P.E	P.E	KCl	P.E	P.E	KCl	P.E	P.E

0.1M	0.0g/L	0	0	0	0	0	0	0	0	0	0	0	0
	0.1g/L	47	81.1	82.5	44.6	81.9	83.9	50	80	83.3	47.6	72.5	75
	0.3g/L	47	84.8	86	44.6	85.8	85.5	50	83.3	83.3	47.6	75	77.5
	0.5g/L	47	86	86.5	44.6	84.9	86.9	50	85	86.6	47.6	80	85
0.3M	0.0g/L	0	0	0	0	0	0	0	0	0	0	0	0
	0.1g/L	62.1	81.1	86	61.4	81.9	86.7	60	80	85.9	56.3	72.5	81.3
	0.3g/L	62.1	84.8	89.5	61.4	85.8	90	60	83.3	90	56.3	75	82.5
	0.5g/L	62.1	86	90.3	61.4	84.9	91.2	60	85	90	56.3	80	87.5
0.5M	0.0g/L	0	0	0	0	0	0	0	0	0	0	0	0
	0.1g/L	71.1	81.1	92.7	68.8	81.9	92	65	80	88.6	62.5	72.5	85
	0.3g/L	71.1	84.8	90.3	68.8	85.8	92.7	65	83.3	91.4	62.5	75	87.5
	0.5g/L	71.1	86	87	68.8	84.9	93.4	65	85	91.4	62.5	80	91.3

210 **Key: P.E (Plant extract); KCl (Potassium Chloride)**

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212

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214 **Table 4. Calculated values of inhibition efficiencies (%) for zinc corrosion in varying HCl,**
215 **plant extract and KI concentrations**

Corrodent Conc.		0.5M HCl			1M HCl			1.5M HCl			2M HCl		
KI	Extract	KI +			KI +			KI +			KI +		
Conc.	conc.	KI	P.E	P.E	KI	P.E	P.E	KI	P.E	P.E	KI	P.E	P.E
0.1M	0.0g/L	0	0	0	0	0	0	0	0	0	0	0	0
	0.1g/L	62.1	81.1	86	57.8	81.9	90	60	80	86.7	53.8	72.5	77.5
	0.3g/L	62.1	84.8	90.3	57.8	85.8	89	60	83.3	88.3	53.8	75	81.3
	0.5g/L	62.1	86	93	57.8	84.9	90	60	85	90	53.8	80	87.5
0.3M	0.0g/L	0	0	0	0	0	0	0	0	0	0	0	0
	0.1g/L	75	81.1	89.5	78.3	81.9	92	63.3	80	90	57.6	72.5	82.5
	0.3g/L	75	84.8	93.5	78.3	85.8	92	63.3	83.3	91.6	57.6	75	85
	0.5g/L	75	86	90	78.3	84.9	94	63.3	85	93.3	57.6	80	90
0.5M	0.0g/L	0	0	0	0	0	0	0	0	0	0	0	0
	0.1g/L	77	81.1	94	79	81.9	93	70	80	91.4	68.8	72.5	87.5

0.3g/L	77	84.8	93.7	79	85.8	93.6	70	83.3	93.3	68.8	75	90
0.5g/L	77	86	93.5	79	84.9	95.2	70	85	92.9	68.8	80	91.4

Key: P.E (Plant extract); KI (Potassium Iodide)

3.6 Synergism

Synergism is a combined action of a compound greater in total effect than the sum of individual effects. It has become one of the most important factors in inhibition process and serves as a basis for all modern corrosion inhibitor formulation. Synergism of corrosion inhibitors is either due to interaction between components of the inhibitors or due to interaction between the inhibitor and one of the ions present in aqueous solution [9, 15]. Synergistic studies were carried out on the combination of the inhibitor-plant extract (0.1, 0.3, 0.5g/L) with KCl, and KI (0.1, 0.3, 0.5M) in HCl (0.5, 1, 1.5, 2M) respectively. Synergism parameter (S) of the inhibitor due to halides was calculated using Equation (3)

$$S = \frac{1 - I_A - I_B + I_{AB}}{1 - I_{AB}} \quad (3)$$

Where I_A and I_B are inhibition efficiencies of the inhibitor and halide, respectively, and I_{AB} is the inhibition efficiency of the inhibitor, when it is combined with halide [9].

S approaches 1 when no interaction between the inhibitor compounds exists. When $S < 1$, the antagonistic interaction prevails. Values of synergism parameters as recorded in table 5 ($S < 1$ in all cases) shows that the adsorption of one compound antagonizes another which results in mass coverage and thus improve efficiency of inhibition [15]. The reason for excellent synergistic combination of halides with plant extract is not farfetched; since it is difficult for the positively charged phytochemical to approach the zinc surface at high acidic concentration due to electrostatic repulsion, presence of anions (Cl^- and I^-) improves the inhibition efficiency as the anions are first adsorbed on the zinc surface making the surface negatively charged as a result of electrostatic attraction, after which the protonated compounds can now effectively reached the Zinc surface, Hence presence of halides (KCl and KI) improves the inhibition efficiency of the plant extract in the order $KI > KCl$ [15].

Table 5. Synergism parameter (S) for plant extracts, halide and plant extract-halide mixture for the corrosion of zinc in HCl solution

Corrodent									
Halide Conc.	Conc.	0.5M HCl		1M HCl		1.5M HCl		2M HCl	
	Extract conc.	KCl	KI	KCl	KI	KCl	KI	KCl	KI
0.1M	0.0g/L	0	0	0	0	0	0	0	0
	0.1g/L	-45.2	-57.6	-42.5	-51.6	-47	-54.3	-45	-49.3
	0.3g/L	-45.4	-60.2	-43.8	-54.7	-49	-55.6	-45.1	-48.7
	0.5g/L	-45.7	-56.5	-42.58	-53.5	-48.1	-55.7	-43.8	-48.2
0.3M	0.0g/L	0	0	0	0	0	0	0	0
	0.1g/L	-57.6	-67	-57	-68.2	-54.9	-55.3	-49.2	-49.7
	0.3g/L	-57.9	-67	-57.5	-72	-54.6	-56.6	-50.2	-49.9
	0.5g/L	-58.2	-70.7	-56.2	-69.7	-55.7	-56.7	-50.5	-50.2
0.5M	0.0g/L	0	0	0	0	0	0	0	0
	0.1g/L	-61.2	-65.5	-60.3	-68.6	-57.7	-60.3	-52.3	-56
	0.3g/L	-65.9	-68.8	-62.7	-71.4	-58.3	-61.5	-52.6	-56.4
	0.5g/L	-69.3	-69.8	-61.6	-69.5	-59.5	-63.1	-53.8	-59.3

Key: KCl (potassium Chloride); KI (potassium Iodide)

3.7 Adsorption studies

The inhibition efficiency of Moringa oleifera extract or the halide additives can be related to the degree of surface coverage (θ) using equations (4) and (5):

$$\%IE = \left[1 - \frac{w_1}{w_2} \right] \times 100 \quad (4)$$

$$\theta = 1 - \frac{w_1}{w_2} \quad (5)$$

Where, w_1 and w_2 are the weight losses (grams) for zinc in the presence and absence of additives respectively in HCl solution at the same temperature [16-17].

From the surface coverage (θ) for different inhibitor concentrations the respective adsorption isotherms can be obtained. The surface coverage data fits into the Langmuir isotherm (fig. 8) represented as,

$$\frac{C}{\theta} = \frac{1}{b} C \quad (6)$$

Where, C is concentration of additives, θ is the surface coverage and b is the Langmuir constant which represents the degree of adsorption affinity for the adsorbate. With either additive, it was shown that corrosion inhibition of zinc obeys the Langmuir isotherm. A plot (C/θ) against C, for all concentrations of inhibitors, a straight line relationship was obtained in all cases with a correlation coefficients (R^2) in the range $1.00 > R^2 > 0.994$. Hence the mechanism of inhibition may be due to the formation and maintenance of a protective film on the metal surface [8], on the platform of chemical adsorption since inhibition increases with temperature increase.

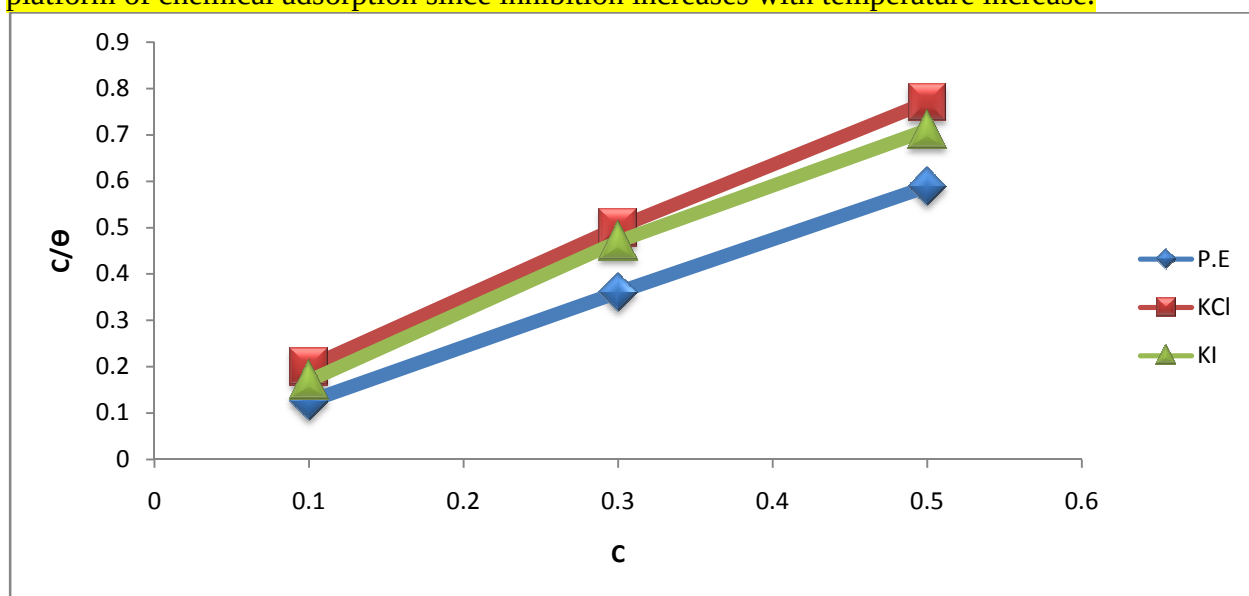


Figure 8: Langmuir isotherm model for the corrosion of zinc in varying plant extract, KCl and KI concentration at 1.5M HCl solution

4. CONCLUSIONS

The used biologically active *Moringa oleifera* leaves extract as corrosion inhibitors for zinc in varying HCl act as an efficient inhibitor. It is concluded that the inhibition efficiency of the extract is due to the presence of saponins, tannins, flavonoids, glycosides, carbonhydrates, reducing sugars, terpenoids, steroids and alkaloids present in the plant extract. Also, the inhibition efficiency increases with the increase in inhibitor concentration and decreases with

increase in corrodent concentration. Adsorption of plant extract, KCl and KI on the Zn surface from acidic solution followed Langmuir isotherm, indicating that the main inhibition process occurred via adsorption (Chemical adsorption). The addition of KI and KCl to these compounds improve the values of inhibition efficiency due to synergistic effect

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