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EFFECT OF CONCENTRATION, CONTACT TIME AND TEMPERATURE ON INHIBITORY POTENTIAL OF GREEN INHIBITORS CASE STUDY: ZEA MAYS COBS EXTRACT ON MILD STEEL

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ABSTRACT

The inhibitive effects of acid extracts of *Zea may s*cobs on the corrosion of mild steel in 1M H_2SO_4 solution were investigated. Experiments were performed by varying immersion period, concentration of the inhibitor and the reaction temperature. The inhibition efficiency of the extract obtained from weight loss method was found to increase with increase in concentration of the extracts. The highest inhibition efficiencies observed was at 0.4 % (v/v) which was 89.68%.The results showed that the corrosion rate of mild steel in 1M H_2SO_4acid decreased with increase in extract concentration. Thermodynamic studies revealed a mechanism of physical adsorption of plant extract on the surface of the metal. The data obtained were fitted into Langmuir isotherm, the energy of activation (E_A) was found to decrease from 22.01kJmol^{-1} to 5.15 kJmol^{-1} with increase in inhibitor concentration of extract. The calculated values of Gibbs free energy are in range of -10.24 kJmol^{-1} to -11.28 kJmol^{-1} for the extract. The Kinetic studies of the reaction process revealed a first order reaction.

KEYWORDS: Zea Mays, Greeninhibitor, Mild Steel, Inhibitory Potential.

INTRODUCTION

Corrosion of metals has become a threat to many industrial operations globally which utilizes metals as source of raw material in building of various plants and machineries[1, 2, 3]. This is due to the facts that some industrial processes such as etching, acid cleaning and pickling catalyze a contact between metal and the reactive mediums (base or acid or salt)[4, 5]. To mitigate this corrosion effect, the use of natural and synthetic corrosion inhibitors has been established but the former is safe, non-toxic and harmless while the latter is toxic and harmful. The natural corrosion inhibitors otherwise known as green inhibitors are environmentally friendly, readily available, biodegradable, cheap and renewable source of materials which make them to be useful as anti-corrosion agents [6].

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The synthetic corrosion inhibitors contain inorganic compounds like molybdates, phosphates, chromates and different varieties of organic compounds containing heteroatoms like Sulphur, oxygen which make them to be unsuitable as corrosion inhibitors, they are not environmental friendly, not easily biodegradable and toxic [7]. They are also difficult to dispose and create permanent environmental pollution. Corrosion inhibitors will reduce the rate of either anodic reaction or cathodic reaction or both. Most of natural corrosion inhibitors have hydroxyl(-OH) group, carboxylic acid (-COOH) group, amide (-$CONH_2$) group etc. which improve their potency as corrosion inhibitors. This study is aimed at investigating the effect of immersion time, concentration and temperature variation and their kinetic studies on the inhibitory potential of Zea mays extract on the corrosion of mild steel in 1M H_2SO_4 solution.

MATERIALS AND METHODS

Materials used for the study were mild steel sheet of composition (wt. %); Si(0.056), C (0.187), Mn(0.474), S(0.039), Al (0.124), Cu(0.198),Fe(98.7). It was sectioned into uniform dimension of 18 x 16 x 4 mm in the Mechanical Engineering workshop of the Federal University of Technology, Akure Ondo, Nigeria before carrying out corrosion test on them. Other materials and equipment include *Zea-mays cobs*, H_2SO_4 acid, distilled water, beakers, emery paper, iron filling, analytical weighing balance (Mettler Toledo PB153), measuring cylinder, thermo stated water bath, thermometer, paper tape, what man filter paper and oven. All the solvents were of analytical grade and redistilled before usage to ensure purity.

EXTRACTION OF PLANT

Sample of *Zea mays cobs* was collected at Oja Oba, Akure, Ondo State. The sample was dried in the sun for 8 weeks, pulverized into fine powders and sieved with 50 m mesh. Initially, 10g of powdered material was dissolved in 100 mL of 1M H_2SO_4 solution.in a round bottom flask. The blank was 100 mL of 1M H_2SO_4 solution. The plant materials were boiled at 90^oC for 3hours in water-bath. After this, the solution was cooled overnight, filtered and stored. From the respective stock solution, inhibitor test solutions were prepared in concentration ranges 0.1-0.4% (v/v) H_2SO_4 solution. Each coupon whose initial weight has already been taken (W_1) was immersed inside the respective concentration of the bank (1M) and the inhibitor solutions for 4 hours after which it was retrieved degreased by washing with acetone, washed with distilled water, dried and weighed (W_2). From the weight loss, corrosion rate (CR) and inhibition efficiency (I. E%) were calculated using equations.

$$CR\ (gh^{-1}cm^{-1}) = \Delta\ W/AT \qquad \textbf{Equation 1}$$

Where CR is the corrosion rate, ΔW is weight loss i.e. W_1-W_2, A is the area of the coupon in cm^2 and T is time in hour.

$$I.E\% = (1 - \frac{CRinh}{CRblank})\ X\ 100 \qquad \textbf{Equation 2}$$

Where CR_{inh} and CR_{blank}correspond to the corrosion rates in the presence and absence of inhibitor respectively.

I.E is the inhibition efficiency.

The surface coveragewas calculated by using equation below.

$$\theta = (1 - \frac{CRinh}{CRblank}) \qquad \textbf{Equation 3}$$

ELECTROCHEMICAL METHOD

Experiments were carried out in a conventional three-electrode cell assembly with working electrode as mild steel specimen of 1cm^{-2} area which was exposed and the rest being covered with red lacquer, a rectangular platinum foil as the counter electrode andthe reference electrode as SCEinstead of salt bridge aluggin capillary arrangement was used to keep SCE close to the working electrode to avoid the ohmic contribution. A time interval of 10-30minutes was given for each experiment to attain the steady state open circuit potential. The polarization was carried from a cathode potential of +250 mV(vsSCE) to an anodic potential of -250 mV (Vs SCE) at a sweep rate of 1mV^{-1}.The inhibition efficiency was calculated using the *formula:*

$$\text{IE }(\%)=\frac{Icorr-I{*}corr\times 100}{Icorr} \qquad \textbf{Equation 4}$$

Where Icorr and I*corr are corrosion current in the absence and presence of inhibitorrer-spectively.

RESULTS AND DISCUSSION

EFFECT OF CONCENTRATION ON CORROSION RATE

Figure 1 show the variation of corrosion rate with varying concentration of the acid extract of Zea mays cobs from 0.1 %(v/v) to 0.4 %(v/v) in 1 M H_2SO_4 acid at different temprature values for 4 hours immersion time respectively. It was observed that the corrosion rate of the blank was higher than that of inhibited solution of the extract as shown in Tables 1. The results that the corrosion rate of mild steel in 1 M H_2SO_4 decreases with increase in concentration of the extract because the extract had been adsorbed on the surface of mild steel and hence, reduction in corrosion rate [8]. As inhibitor concentration increased from 0.1% to 0.5 %v/v, corrosion rate reduced drastically in the temperature range studied. The corrosion rate of mild steel in the blank acid was highest at 343k with a value of 0.0333gcm^{-2}h^{-1} but reduced to 0.00102gcm^{-2}h^{-1} in the presence of 0.4% v/v (AEZMC), as shown in Tables 1. From the values of the inhibition efficiency, it is evident that the corrosion inhibition may be due to adsorption of the plant constituents on the metal surface.

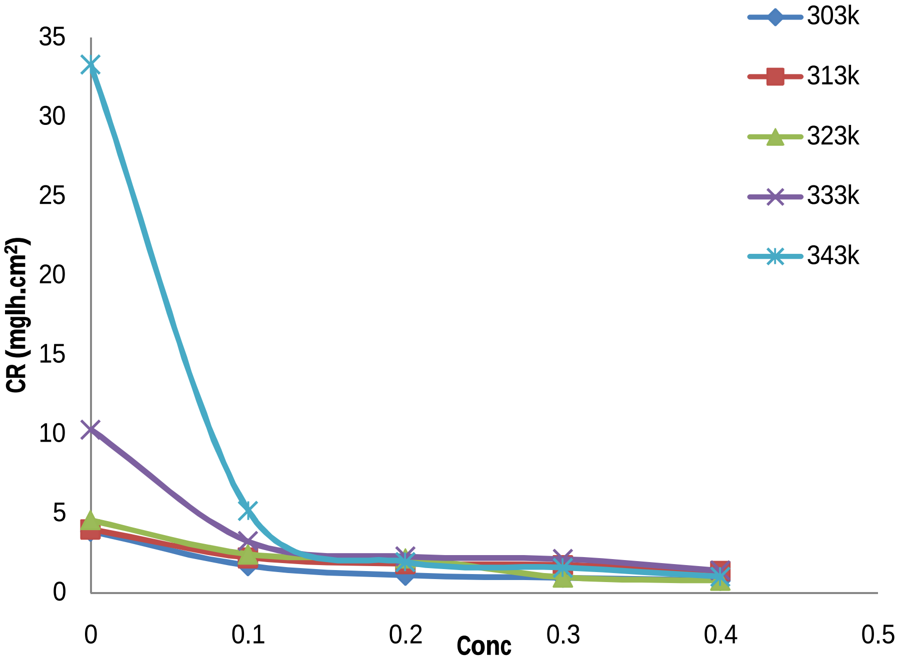

Figure 1.Variation of corrosion rate with varying concentration of the acid extract of Zea mays cobson mild steel in 1M H_2SO4 for 4 hours at different temperatures

Table 1.Corrosion rate of mild steel invarious concentration of AEZMC in 1M H_2SO_4 at different temperatures

Concentration of Acid extract of Zea-mays cobs (%v/v)	Corrosion Rate (gcm^{-2} h$^{-1)}$				
	303k	313k	323k	333k	343k
	0.00389	0.00402	0.00460	0.01032	0.03331
0.1	0.00270	0.00222	0.00244	0.00371	0.00523
0.2	0.00244	0.00184	0.00228	0.00232	0.00192
0.3	0.00210	0.00174	0.00205	0.00211	0.00153
0.4	0.00184	0.00139	0.00184	0.00141	0.00102

EFFECT OF CONCENTRATION ON INHIBITIONEFFICIENCY

Inhibition efficiency values were found to increase with increase in concentration of the extracts and decrease with temperature (Figure 2). Inhibition efficiency of 89.68% (Table 2) was obtained with AEZMC concentration of 0.4% (v/v) at 343K.and increase in inhibition efficiency with decrease with temperature is suggestive of physio sorption of the inhibitor components onto the mild steel surface [9]. Corrosion rate is a function of weight loss. The corrosion rate of mild steel was observed to increase with increase in temperature both in blank solution and in solution containing different concentrations.

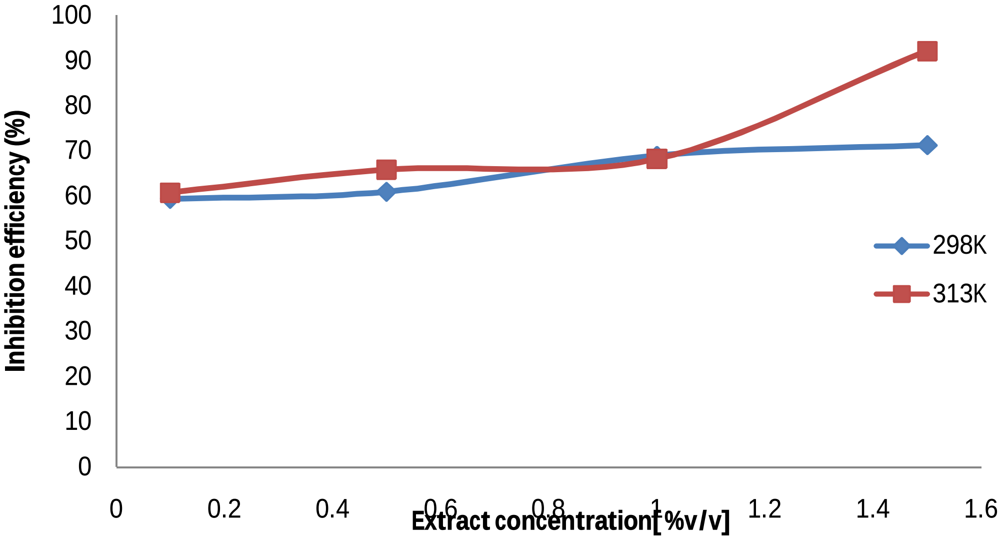

Figure 2.Inhibition Efficiency of different concentrations of zeamays cob on Mild Steel in aqueous solution of 1M H_2SO_4 for 3 hours at room temperature

Table 2.Percentage inhibition efficiency of Zea mays cobs on mild steel in 1M H_2SO_4 at different temperatures

Concentration of Acid extract of Zea-mays cobs (%v/v)	Inhibition Efficiency (%)				
	303k	313k	323k	333k	343k
0.1	50.16	51.09	54.45	65.11	71.12
0.2	58.21	60.23	61.06	73.23	74.81
0.3	74.89	64.61	79.11	79.16	79.66
0.4	78.34	78.81	81.21	85.66	89.68

EFFECT OF TEMPERATURE ON CORROSION RATE

The effect of temperature on corrosion rate was studied for the acid extracts of Zea *mays cobs* to evaluate the stability of adsorbed layer/ film of inhibitor on mild steel surface. Weight loss measurement were carried out in the temperature range of 303-343K in absence and presence of the inhibitor. Figure 3 plots revealed increase in corrosion rate with increase in temperature. [8] reported the increase in corrosion rate with temperature is due to increase in average kinetic energy of the reacting inhibitor molecules It was found that the rate of mild steel corrosion, in free and un-inhibited acid solution, increases with increase in temperature but the corrosion rate is much decreased for inhibited acid solution than the un-inhibited acid solution.

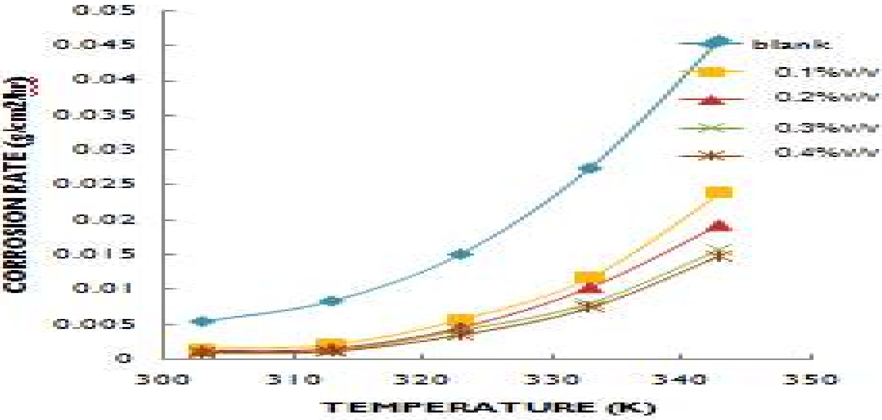

Figure 3.Plots revealed increase in corrosion rate with increase in temperature

EFFECT OF TEMPERATURE ON INHIBITION EFFICIENCY

Figure 4 shows how inhibition Efficiency (I.E) varies with temperature in different concentrations of (AEZMC). I.E values were found to decreases with increase in concentration of the extracts and temperature. Inhibition efficiency of 96.93% was obtained with extract concentration of 0.4% v/v at 343k.These results suggest a physical adsorption of the extract compounds on the mild steel surface.A similar observation was reported by [9].

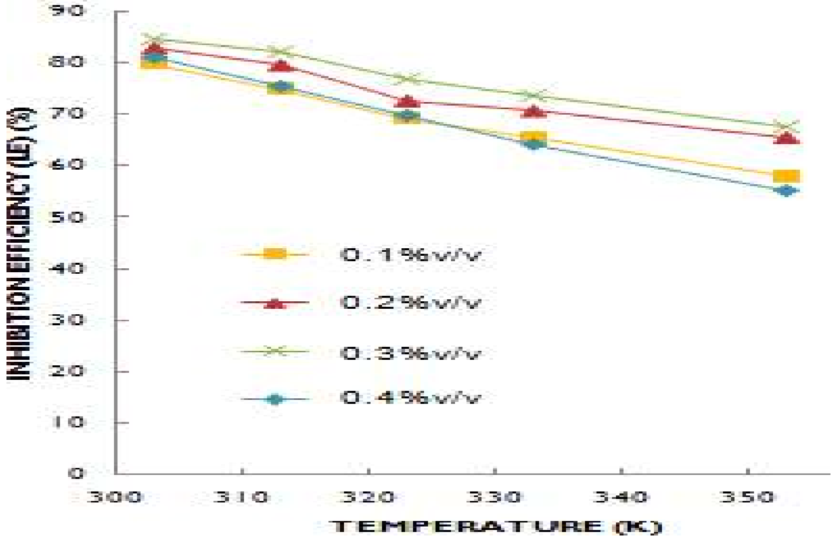

Figure 4.Variation of inhibition efficiencies of acid extract of Zea-may cob (AEZMC) with temperature on mild steel in 1 M H_2SO_4

KINETIC STUDIES

The data obtained from the variation of weight loss against time with respect to extract concentration were fitted into equation (5) to test for the order of corrosion reaction.

$\text{In}\,(W_{i}\text{-}\,\Delta W) = -kt + \text{In}W_{i}$ **Equation 5**

Where W_i is the initial weight of metal, ΔW is the weight loss or change in weight at time "t" is the immersion time and k the rate constant. The plots for the first order reaction in different concentrations of the inhibitors are shown in Figure 5 which indicate that a first order Kinetic is applicable to the corrosion of mild steel in the presence or absence of the inhibitor. In addition, the half-lives ($t_{1/2}$) of the corrosion of mild steel in various media were calculated using equation 6

$t_{1/2} = \frac{0.693}{k}$ **Equation 6**

Values of rate constant (k) obtained from the slope of the plots of equation 5and the half-lives calculated using equation 6are presented in Table 5. From the results obtained, it is significant to note that half-life increases with increase in the concentration of the extracts.

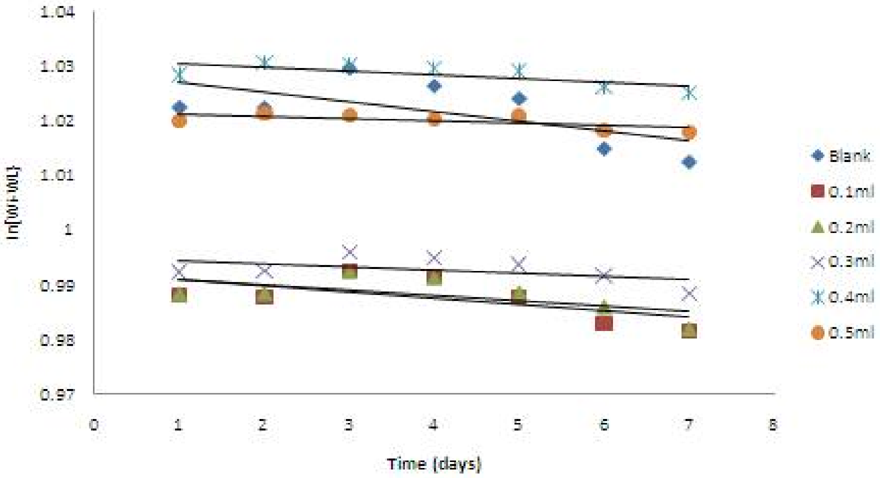

Figure 5.A plot of In (Wi – W) against time for the adsorption of AEZMC on mild steel at room temperature

Table 5.The values of rate constant (k) and half-life (t1/2) for mild steel in 1M h2so4 in the absence and presence of different concentrations

Rate constant k of half-life (t1/2),		
Conc. (%v/v)	**AEZMC (day^{-1} x 10^{-3})**	**(day^{-1}) AEZMC**
Blank (0%)	41.83	166
0.1%	2.74	252
0.2%	2.28	303
0.3%	1.57	440
0.4%	1.32	525
0.5%	1.02	673

THERMODYNAMIC STUDIES

The logarithm of corrosion rate is a linear function of temperature (Arrhenius equation).

$\text{Log}\,(C_R) = \frac{-Ea}{2.303RT} + \text{Log}\,A$ **Equation 7**

Where E_a is the apparent activation energy, R is the general gas constant and A is the Arrhenius pre-exponential factor. A plot of logarithm of corrosion rate obtained by weight loss measurement versus 1/T gave a straight-line graph as shown in Figures 6.The slope of –Ea/2.303R.[11] gave the relationship between the temperature. The values of activation energy, enthalpy change, entropy change obtained in this study are listed in Table 7. The activation energy in the inhibited solution decreases from 22.01 to 5.15kj/mol with increase in inhibitor concentration for acid extract of AEZMC. Meanwhile, Ea values of the blank are higher than values obtained for a system containing various concentrations of AEZMC. This result indicated that AEZMC extract is adsorbed on the surface of mild steel by physical adsorption. The positive values of ΔH both in the absence and presence of the extracts reflect the endothermic nature of the mild steel dissolution process. The shift towards negative values of entropies (ΔS) implies that the activated complex in the rate determining step represents association rather that dissociation, meaning that disordering reduces on going from reactants to activated complex.

This equation can also be expressed as follows:

$\Delta G_{ads} = -2.303RT \text{ Log } (55.5K_{ads})$ **Equation 8**

Where ΔGads is Gibbs free energy of adsorption, R is the universal gas constant with a value of 8.314 $Jmol^{-}K^{-1}$, T is the temperature in Kelvin and Kads is the equilibrium constant for the adsorption process and 55.5 is the molar concentration of water in solution. K_{ads} values for the inhibitor was calculated from the intercepts of Figures 8. The ΔG_{ads} values, calculated using Equation (13), are also presented in Table 8. The calculated ΔG_{ads} values were in the physio-sorption range from -10.24 to -11.28 kj/mol for AEZMC extract. The modes of adsorption observed could be attributed to the fact that AEZMC contains many different chemical compounds in which some can adsorb physically on the metal surface.

The negative values of Gibbs free energy connote the spontaneity of adsorption process and stability of the adsorbed layer on the surface of mild steel [12].The values of ΔG_{ads} are below -40 kJ/mol indicating that the inhibitors function by physically adsorbing on the surface of the metal. Generally, values of ΔG_{ads} up -20 kJ/mol are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption) while those more negative than -40 kJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates physio-sorption process).

Table 7.Calculated values of activation parameters for mild steel corrosion 1M H2SO4 containing AEZMC

Conc %(v/v)	**Ea (KJ mol^{-1}) AEZMC**	**ΔH (KJ mol^{-1}) AEZMC**	**ΔS (KJ $mol^{-1}K^{-1}$) AEZMC**
Blank	43.8498	42.2206	-95.396
0.1	22.0097	30.2619	-204.644
0.2	11.8031	28.4238	-234.611
0.3	10.6664	15.2955	-231.231
0.4	5.1534	12.1032	-359.792

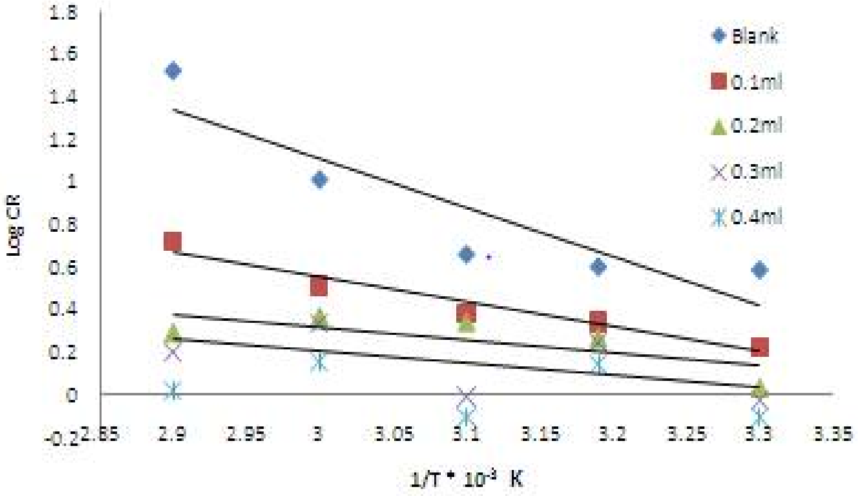

Figure 6.Arrhenius plot for mild steel in 1M H2SO4 in the absence (Blank) and presence of Zea mays cobs (AEZMC)

Table 8.The values of Equilibrium constant and energy of adsorption for mild steel corrosion in 1M H2SO4 for AEZMC at different temperatures

Temperature (Kelvin)	**Adsorption Constant of AEZMC (kads)**	**Gibbs Free energy, ΔG of AEZMC, (KJ/mol)**
303	1.0507	-10.2444
313	1.3390	-11.2134
323	0.9306	-10.5944
333	1.0431	-11.2386
343	0.9425	-11.2866

LANGMUIR ISOTHERM

Langmuir isotherm is ideal for physical or chemical adsorption where there is no interaction between the adsorbed and the adsorbent. It is represented by Equation 9 as follows [13]:

$$\frac{Cinh}{\theta} = \frac{1}{Kads} + C_{inh} \qquad \textbf{Equation 9}$$

The plots of C_{inh}/θ vs. C_{inh} yielded straight lines for the inhibitor as shown in Figures 9.The best fit for this study was obtained with Langmuir isotherm (with strong correlation coefficient R^2 □ 1 at all the temperatures of study). This indicates that the adsorption Zea *may s*cobs extract occupy typical adsorption site at the metal/solution interface. Langmuir Isotherm characterizes physio sorption of the adsorbed species and postulates monolayer adsorption of the adsorbate onto the adsorbent which is expected to have a slope of unity [14]. The slope of unity obtained in this study is an indication that the adsorption of the extract components is approximated by Langmuir adsorption isotherm and that monolayer of the inhibitor species must have been attached to mild steel surface without lateral interaction between adsorbed species.

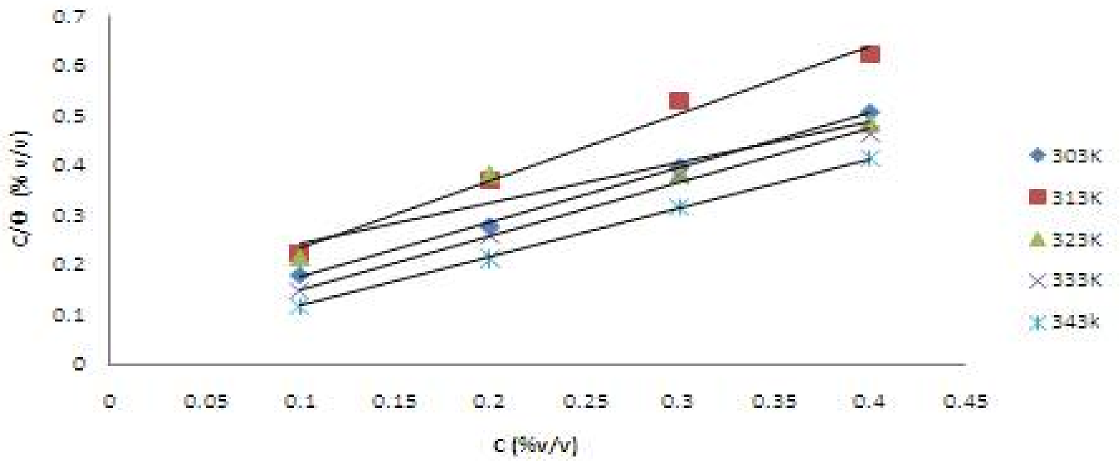

Figure 9.Langmuir adsorption isotherm plot for mild steel corrosion in 1M H2SO4 for acid extract of Zea mays cob (AEZMC) at different temperatures

The values of k_{ads} revealed that adsorption coefficient increases with increase in temperature. The adsorption constant, R^2 values and slope of the Langmuir plots of the inhibitor are given in Table 9

Table 9.Calculated parameter from Langmuir adsorption isotherm plot for AEZMC

Temperature (K)	Slope	RValue	Adsorption constant kads
303	1.1082	0.9994	15.8931
313	1.3592	0.9946	17.3873
323	0.8094	0.9363	19.1732
333	1.0728	0.9925	23.0915
343	0.9858	0.9998	26.5556

POTENTIODYNAMIC POLARIZATION STUDY

Polarization measurements were made to evaluate the corrosion current density, corrosion potential and Tafel slope. From the polarization curves shown in Figure10. It will be observed that, the presence of the extracts lower the current density (i_{corr}) values of*Zea mays* cob from 22.87 mA/cm^{-2}(blank) to 1.21mA/cm^{-2} shown in Table 10 without causing any significant change in corrosion potential (E_{corr}) suggesting that these extracts are a mixed type inhibitor. Tafel slopes (ba and bc) for mild steel in the presence of the inhibitor change uniformly. This behavior indicated that the inhibitor is adsorbed on both the anodic and cathodic sites. Tafel slope (ba and bc), corrosion potential (E_{corr}) and corrosion current(I_{corr}) were presented in Tables 15

Table 10.Calculated parameters from potentiometric polarization measurements for AEZMC

Conc. % (v/v)	Corrosion rate (mm/Year)	-E_{corr} (mV)	I_{corr}(mA/cm^{-2})	b_2(mV)	B_2(mV)	IE (%)
Blank	25.97	-443.28	22.87	190.32	369.39	…..
2	7.26	-427.46	6.39	58.53	193.89	72.05
4	6.53	-415.86	5.75	45.98	209.36	74.85
6	4.91	-426.03	4.32	52.26	174.94	81.11
8	3.54	-427.79	1.36	57.56	162.72	94.05

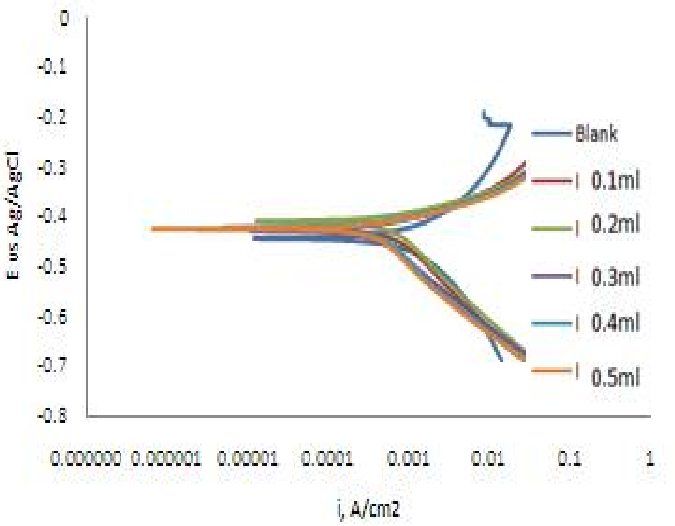

Figure 10.Potentiodynamic polarization curve for mild steel in 1M H2SO4 without and with various concentration of the AEZMCd steel in acid medium

CONCLUSION

The study has shown that crude extract of Zea mays cob act as inhibitor for mild steel corrosion in acidic medium.Inhibition efficiency of the extract increases with increase in concentration of the inhibitor and decreases with temperature. Also, it was observed that the immersion time has influence on the inhibition efficiency. It was observed that the increase in contact time gave inhibition efficiency. The extract was found to best obey Langmuir adsorption isotherm within experimental data at the concentrations and temperature ranges studied. The values of ΔG^{o}_{ads}obtained are low and negative, which reveals the spontaneity of the adsorption process and further support the physical adsorption mechanism.

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