



ANTI-CORROSION INHIBITION OF ZINC IN 1M HYDROCHLORIC ACID SOLUTION BY USING *Azadirachta Indica* FRUITS LATEX (AIL)

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ABSTRACT

Anticorrosion activities of *Azadirachta Indica Latex* (AIL) as a corrosion inhibitor of zinc in 1.0M HCl were investigated using weight loss, FT-IR spectroscopy and scanning electron microscopy (SEM). The weight loss results show that corrosion of zinc in blank media increases with an increase in the time of immersion, concentration and temperature. AIL was found to be a highly effective inhibitor in 1.0M HCl with a minimum inhibition efficiency of 98.45% obtained from 0.1% inhibitor concentration at 318K. Adsorption of AIL on zinc obeys Langmuir adsorption isotherm. The results of the isotherm, FT-IR spectra and the values obtained for ΔG°_{ads} in this study reveal physisorption controlled mechanism for the adsorption of AIL on the zinc surface. The SEM results also confirmed the adsorption of AIL on the zinc surface. The search for cheap and eco-friendly corrosion inhibitors is the aim of this research. The results obtained revealed that, AIL is highly efficient inhibitor for zinc metal and it can be apply to protect it in highly acidic environment.

Keywords: Corrosion, Zinc, Hydrochloric Acid, Inhibitor, *Azadirachta Indica*

INTRODUCTION

Exceptional properties of metals such as conductivity, high tensile strength, durability, malleability and high melting points have placed advantages on their applications over non-metals. Despite these properties, all materials made of metals are subject to corrosion during use and are therefore susceptible to deterioration and degradation processes (Rafael *et al.*, 2014). Corrosion leads to partial or total replacement of equipments and affected structures as such, it imposes huge economic losses to industries and society at large. These factors necessitated the development of processes to control corrosion. Early efforts of controlling corrosion involved the use of inorganic corrosion inhibitors (CIs) such as salts of heavy metals and inorganic anions (Bethencourt, 1998). The ability of organic inhibitors to form protective layers on the metal surface in media with high hydrocarbons made them as a good choice for corrosion protection in petroleum refining processes (Olivares *et al.*, 2006). These inhibitors despite their performances posed hazards on to the environment. This factor and the need to develop cheap, non-toxic and environmentally friendly processes led to the development of green corrosion inhibitors. This development focused on extract from plants, ionic liquids, bio-chemicals and biodegradable substances (Camila and Alexandre, 2014; Nabel *et al.*, 2013). Common in the study of corrosion inhibition is the use of solvent extract from plants but the indiscriminate release of solvents into the environment after extraction has called for a global concern due to health risks posed to lives. Ethanol which is a common extracting solvent is not left out in the list of these health-threatening solvents (Sanni and Mutta, 2014). One of the green corrosion inhibitor is *Azadirachta indica*. Its leaf extract provides a highly efficient (89.25%) inhibition, and serve as a strong anti-cracker and anti-pitting agent against HCl on mild steel. Kumar *et al.*, 2022). *Caesalpinia Crista* has shown 99.4% inhibition efficiency in mass loss of Zinc when immersed in HCl (Abdallah *et al.*, 2014). In this work latex obtained from fresh

fruits of *azadirachta indica* was used as a corrosion inhibitor. The adsorption and corrosion inhibition effect of AIL was investigated using the weight loss method, Fourier Transform Infrared Spectroscopy (FT-IR) and Scanning Electron Microscopy (SEM).

MATERIALS AND METHODS

Material Preparation

Analytical grade Zinc sheet of purity 99.9% and thickness 0.38 mm was mechanically pressed-cut into coupons each of dimension 2.5×2.5×0.038 cm. Each coupon was polished with abrasive paper, washed with de-ionized water, degreased with acetone and dried at room temperature.

Test solution

The solution of 1M hydrochloric acid (Test solution) was prepared for each experiment using analytical grade of hydrochloric acid (36%) and diluted with de-ionized water. The concentration range of the inhibitor was 0.1% (v/v)-0.5% (v/v).

Preparation of AIL

Fresh *azadirachta indica* fruits were collected from the premises of Bayero University Kano, Nigeria. The fruits were washed with distilled water and pressed to obtain the milky sap (Latex). The latex was kept in a clean dry bottle, corked and stored at room temperature.

Methods

Weight Loss Method

The mass weight loss measurements were conducted under total immersion of zinc coupon using 150cm³ capacity beakers each containing 100 cm³ test solution. The temperature maintenance was achieved using a thermostatic water bath. The temperature range chosen for this study was 298K - 318K. The weights of the zinc sample before and after each test were determined using Wincom FA 2004 analytical

balance. From the weight loss, the corrosion rates and other parameters were calculated as follows;

$$W_o = wf - wi \tag{1}$$

Where W_o is weight loss, wi and wf are weights of the coupon before and after immersion respectively.

$$CR = \frac{W_o}{t \times A} \tag{2}$$

Where CR is the corrosion rate, t is the time of immersion and A is the total surface area of the zinc coupon.

$$\theta = \frac{R_f - R_i}{R_f} \tag{3}$$

Where θ is the degree of surface coverage, R_i and R_f are rates of corrosion in inhibited and free media respectively.

The inhibitory effect of the inhibitor is estimated as percentage efficiency using the equation;

$$\%I.E = \frac{R_f - R_i}{R_f} \times 100 \tag{4}$$

FT-IR Spectroscopy Study

The natures of the films formed on the surface of the Zinc after immersion in 1.0M HCl in the absence and presence of inhibitor (0.5% v/v) were studied. The specimens were taken out after immersion and the films on the metal surface were analyzed using FT-IR spectroscopy (Carry 638 by Agilent technologies).

Scanning Electron Microscopy (SEM)

Zinc specimens were immersed in 1.0M HCl in the absence and presence of inhibitor (0.5%v/v). The specimens were

taken out after immersion and dried. The surface morphology of the metal was examined using scanning electron microscopy (MODEL-PHENOM prox).

RESULTS AND DISCUSSION

Evaluation of AIL as Corrosion Inhibitor in 1M HCl Solutions

From the weight loss measurements, the corrosion rate (CR), surface coverage, θ and Inhibitor efficiency (I.E%) for various concentrations of AIL, after 3 hrs of immersion at the temperatures of 298K, 308K, 313K and 318K were calculated using equations 1,2 and 3 respectively.

From Fig. 1, it is observed that the value of CR increase with an increase in the temperature of the blank acid solution. In the presence of AIL, the rate of corrosion decreases. At all temperatures, the corrosion rate tends to zero even at the lowest inhibitor concentration (0.1% v/v), an indication of strong adsorption of AIL on the zinc surface. The increase in the area of surface coverage also suggests that AIL strongly adsorbs on the metal surface.

From Table 1 It can be observed that the values of I.E% gradually increase with an increase in the concentration of AIL, the minimum value of I.E% obtained is 98.45% at the lowest concentration (0.1%) and maximum temperature (318K) of the study. The results show that the AIL is a highly effective inhibitor for zinc even at high temperature.

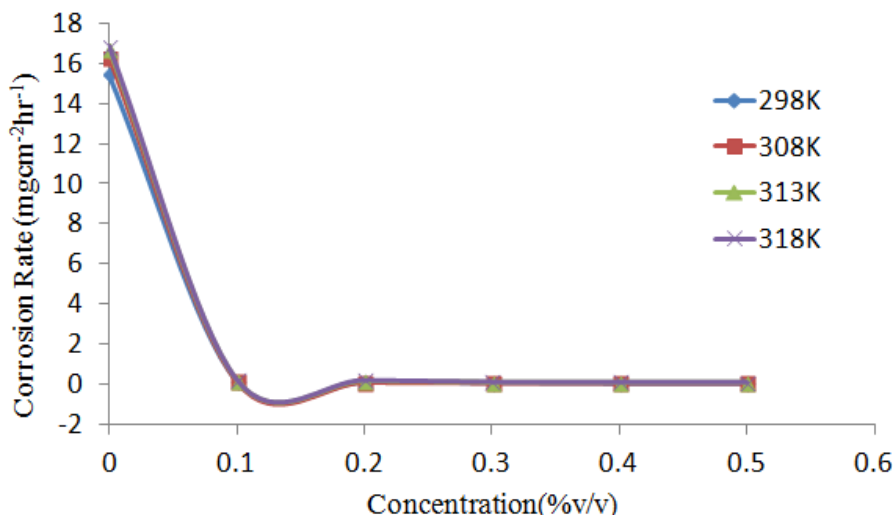


Figure 1: Variation of corrosion rate with concentration

Table 1: Change in θ and %I.E of AIL in 1.0M HCl solution

Inhibitor Conc.	θ (298K)	%I.E (298K)	θ (308K)	%I.E (308K)	θ (313K)	%I.E (313K)	θ (318K)	%I.E (318K)
0.1%	0.990	99.09	0.991	99.06	0.987	98.74	0.985	98.45
0.2%	0.994	99.46	0.994	99.38	0.991	99.10	0.987	98.68
0.3%	0.996	99.61	0.996	99.56	0.994	99.43	0.992	99.19
0.4%	0.999	99.87	0.996	99.60	0.995	99.46	0.992	99.23
0.5%	0.999	99.88	0.996	99.62	0.995	99.49	0.993	99.26

Thermodynamic activation parameters

Arrhenius equation shows the dependence of corrosion rate on temperature (Fouda et al, 2014).

$$\log CR/T = \{ \log(R/hN) + (\Delta S^*/2.303R) \} - (\Delta H^*/2.303RT) \tag{5}$$

Where CR is the corrosion rate, T is the absolute temperature, E_a is the apparent activation energy, R is the molar gas

constant and λ is the frequency factor. A plot of log of CR obtained from gravimetric measurements versus $1/T$ gives a straight line with a regression coefficient close to unity. The values of apparent activation energy (E_a) and pre-exponential factor were calculated from the slope and intercept of the straight lines obtained in the Arrhenius plot and the results are given in Table 2.

The data indicate that the thermodynamic activation energy (Ea) of the corrosion of zinc in 1M HCl containing AIL is higher than those obtained in the free media. These results indicate that the AIL retards the corrosion of zinc in the examined medium.

The transition state equation is given as;

$$\log CR/T = \{ \log(R/hN) + (\Delta S^*/2.303R) \} - (\Delta H^*/2.303RT) \quad (6)$$

Where h is Planck's constant, N is Avogadro's number, ΔS* is the entropy of activation and ΔH* is the enthalpy of activation Fouda et ai, 2014). A plot of log CR/T versus 1/T

gives a straight line with a slope of $-\Delta H^*/2.303R$ and the intercepts of $\log R/hN + \Delta S^*/2.303$, the values of ΔS* and ΔH* were calculated and listed in Table 2. The positive sign of enthalpies reflects the endothermic nature of the zinc dissolution process meaning that the dissolution of zinc was difficult. The negative values of activation entropies show that the activation complex in the rate-determining step represents an association rather than a dissociation step. This means that a decrease in disordering takes place on going from reactants to the activated complex (Kumar et al, 2022).

Table 2: Activation parameters for the dissolution of Zinc in 1.0M HCl containing AIL inhibitor at different concentrations

Concentration(v/v)	Ea (kJ/mol)	ΔH* (kJ/mol)	ΔS* (J/mol/K)
0%	3.621	1.065	-218.584
0.1%	24.566	22.019	-188.044
0.2%	37.950	35.403	-147.739
0.3%	39.213	38.581	-95.142
0.4%	72.549	70.002	-41.759
0.5%	76.091	73.544	-30.884

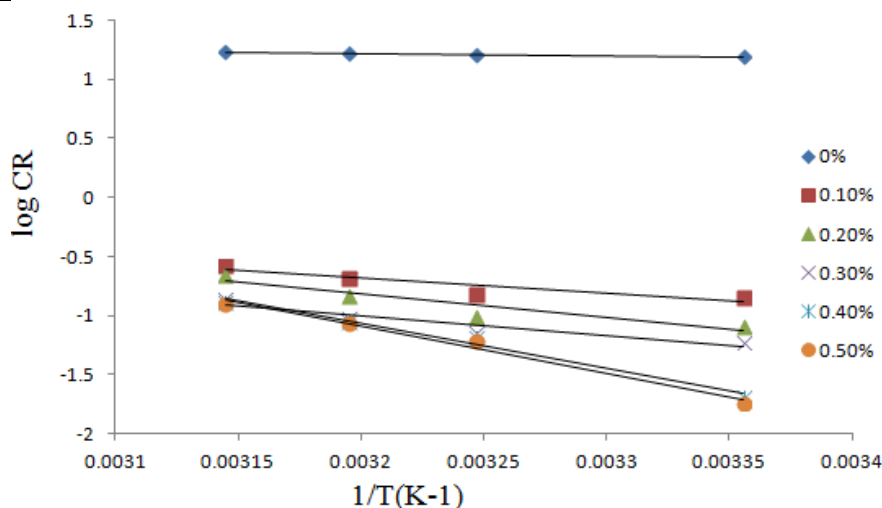


Figure 2: Arrhenius plot for corrosion of zinc in 1M HCl in the absence and presence of different concentrations of AIL

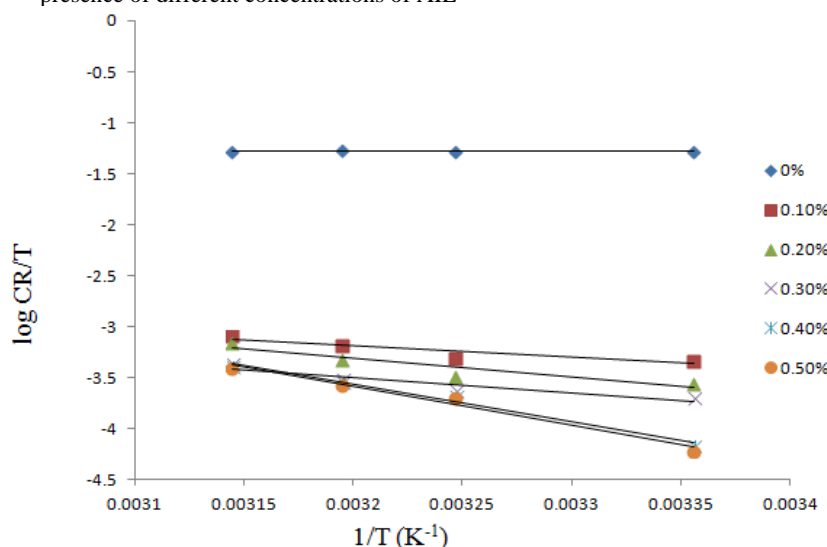


Figure 3: Transition state plot for corrosion of zinc in 1M HCl in the absence and presence of different concentrations of AIL.

Adsorption isotherm

Adsorption of inhibitor is influenced by the nature and the charge of the metal, the chemical structure of the inhibitor, the distribution of the charge in the molecule and the type of electrolyte (Rafael *et al.*, 2014). In this study, the surface coverage (θ) of inhibitors was found to increase with the inhibitor concentration, which is attributed to more adsorption of inhibitor molecules onto the zinc surface. The adsorption mechanism of AIL on zinc was investigated using six adsorption isotherms and the results obtained are presented in Table 3, it was found that AIL obeyed Langmuir adsorption isotherm in an acidic medium. The equation of this adsorption isotherm is given by;

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (7)$$

Where C is the inhibitor concentration in the electrolyte and K_{ads} is the equilibrium constant for the adsorption/desorption process. The surface coverage (θ) values were calculated using mass loss data and the values of C/θ were plotted against

C . These plots are linear with a slope equal to unity. The value of K_{ads} is related to the standard free energy of adsorption, ΔG^0_{ads} by the following equation,

$$\Delta G^0_{ads} = -RT \ln(55.5 \times K_{ads}) \quad (8)$$

Where R is the gas constant, T is the Absolute temperature. The value of 55.5 is the molar concentration of water in solution expressed in mol^{-1} concentration.

The negative values of ΔG^0_{ads} suggest that the adsorption of the inhibitor on the zinc surface is spontaneous. Generally, ΔG^0_{ads} values between 0 and -20kJ/mol are associated with electrostatic interactions between the charged molecules and charged metal surface (physisorption). The values of ΔG^0_{ads} around -40kJ mol^{-1} or more negative involve charge sharing or transfer of charge from the inhibitor molecules to the metal surface to form a coordinate-covalent bond (chemisorption) (Desai *et al.*, 2024). The values obtained for ΔG^0_{ads} in this study (-27 to -28 kJ mol^{-1}) reveal a physisorption controlled mechanism for the adsorption AIL on the zinc surface.

Table 3: Thermodynamic parameters for adsorption of AIL on Zinc in 1.0M HCl solution

Temperature (K)	K_{ads}	ΔG^0_{ads} (kJ/mol)	Langmuir	Freundlich	(R^2) Flory-Huggins	El-Awardy	Temkin	Frumkin
298	1000	-27.065	1	0.981	0.889	0.890	0.981	0.976
308	1000	-27.974	1	0.953	0.977	0.977	0.953	0.971
313	1000	-28.428	1	0.950	0.953	0.954	0.950	0.976
318	1000	-28.882	1	0.917	0.905	0.906	0.917	0.965

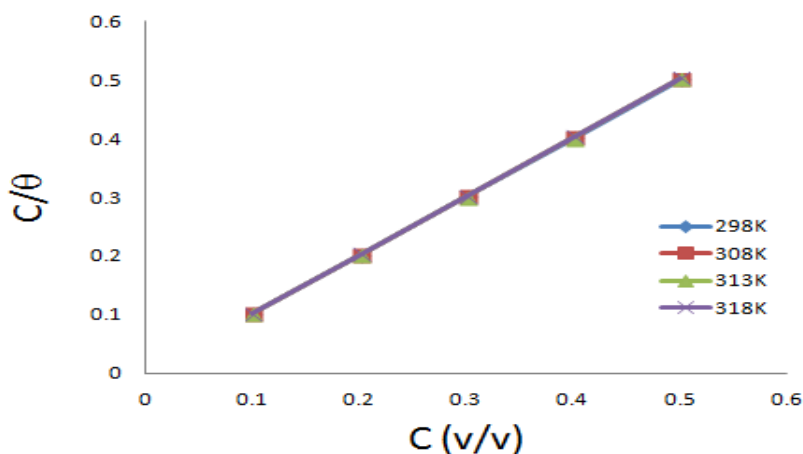


Figure 4: Langmuir adsorption plots of zinc in 1M HCl solution containing different concentrations of AIL

Analysis of FT-IR spectra

The FTIR spectrum of AIL as shown in Fig. 6 reveals the presence of $-\text{OH}$ or $-\text{NH}$ with a broad band at 3257 cm^{-1} . A peak observed at 1641 cm^{-1} is attributable to $-\text{C}=\text{O}$ stretching frequency. Absorption bands indicating the presence of aliphatic and aromatic C-H groups were observed below

1000cm^{-1} . Slight shifts in these values of the adsorption band were observed from the spectra of the film formed on the surface of the metal after the addition of AIL inhibitor. This is attributed to the interaction between the metal and the inhibitors' active centres.

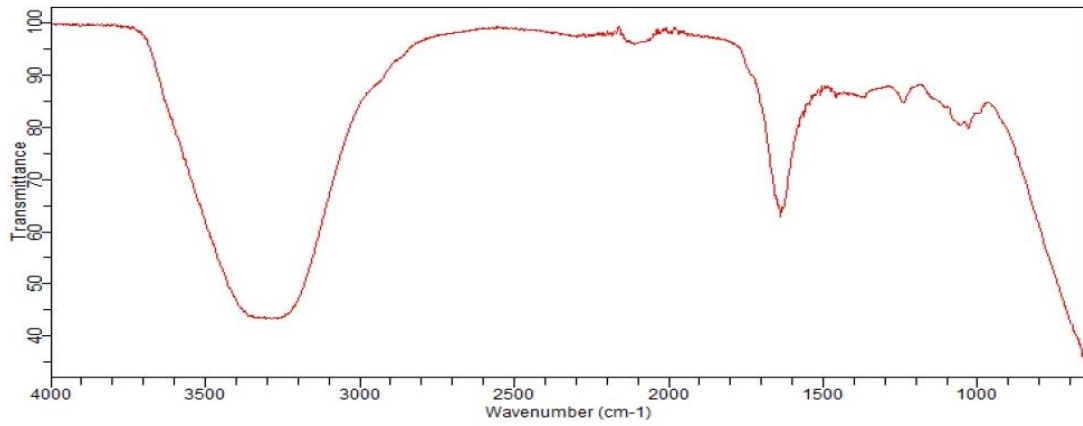


Figure 5: FT-IR Spectra of AIL

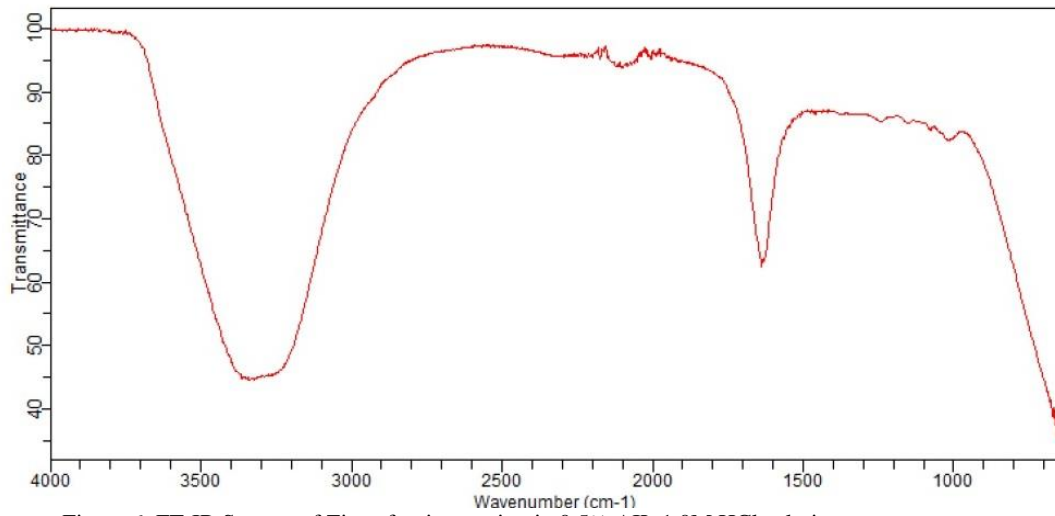
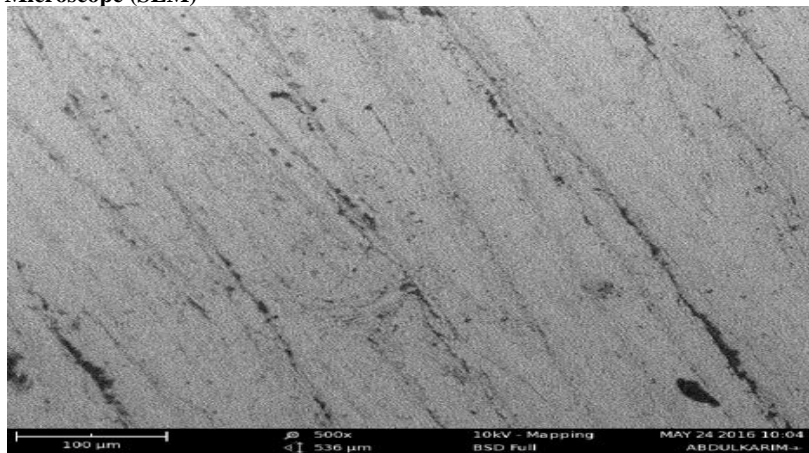


Figure 6: FT-IR Spectra of Zinc after immersion in 0.5% AIL 1.0M HCl solution

Scanning Electron Microscope (SEM)



(a)

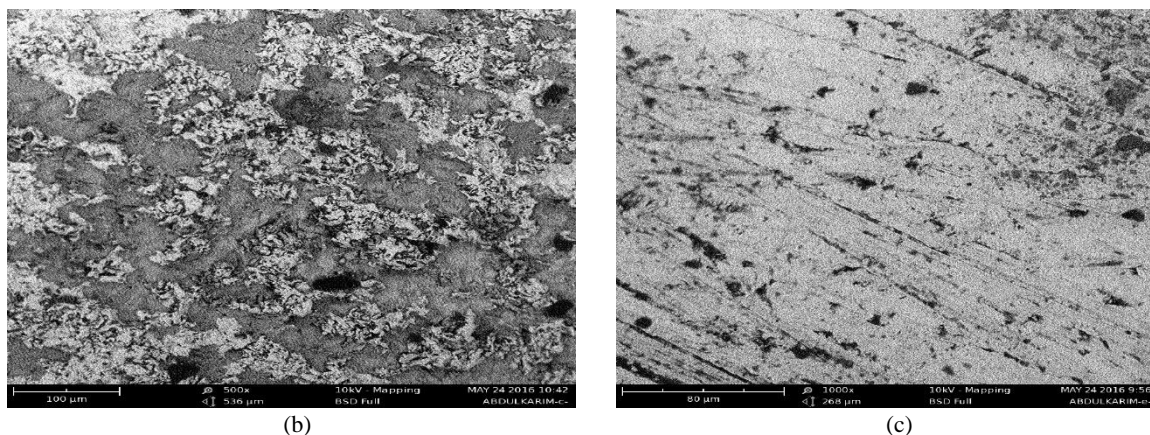


Figure 7a: shows the surface of zinc. Figure 7b: reveals the severe damage on the surface of zinc due to corrosion in 1.0M HCl. Figure 7c: The extent of surface damage reduce by the addition of AIL inhibitor

This result indicates that the corrosion rate is reduced in the presence of the inhibitor. This is due to the adsorption of inhibitor molecules on the metal surface as a protective layer.

CONCLUSION

Anti-corrosion activities of *Azadirachta Indica Latex* as an inhibiting agent on Zinc were studied through the weight loss method. The study reveals the inverse dependence of inhibition on the temperature with the inhibition efficiency of the AIL increasing from a few percentages to a maximum of 98.45% at 1M of HCl. It also shows a direct dependence on inhibitor concentrations. The adsorption of the studied inhibitor agrees with Langmuir adsorption isotherm, SEM images indicate the possibility of formation of the film on the zinc surface while FT-IR spectra reveal that the inhibitor was adsorbed on the metal surface. At all temperatures, AIL is an effective inhibitor of zinc. Latexes of plants showed relatively high inhibition efficiency and reduced the indiscriminate release of toxic solvents into the environment. The mobility of surface charges of these green-inhibited conducting material (metals or semiconductors) increases (Bouklah et al.2006) thus enhancing their stability and conducting efficiency.

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