RESEARCH ARTICLE OPEN ACCESS

Comparative Study of Inhibitive Properties of Pawpaw, Mango Leaves and Cowdung on the Corrosion Behaviour of Api 5l Steel In 0.5 M Hcl And 0.5 M H_2so_4

O .A. Olaseinde
Department of Metallurgical and Materials Engineering, Federal University of Technology, Akure, Nigeria,

ABSTRACT
Failure resulting from the inability of metals to support designed load requirements due to losses imposed by corrosion effects can be combated economically through the aid of chemical inhibitors. Synthetic Inhibitors have been proven to be effective solution in mitigating the problems arising from corrosion of metals but as a result of high cost, disposal and toxicity of the inhibitors, green inhibitors are used as substitutes to synthetic inhibitors. Therefore, a comparative study was carried out on the inhibitive properties of some selected agro wastes (pawpaw leaves, mango leaves and cow dungs) on corrosion behavior of API 5L steel in 0.5 M sulfuric acid and 0.5 M hydrochloric acid. The study was carried out using weight loss measurements, inhibition efficiency and Fourier transform infrared spectroscopy (FTIR). Generally, the agro wastes inhibits the corrosion of the API5L samples in 0.5M H_2SO_4 and 0.5M HCl. The inhibitors are more effective in 0.5M HCl.
Keywords: Corrosion, Inhibitors, agro wastes

Date Of Submission: 09-05-2019 Date Of Acceptance: 24-05-2019

I. INTRODUCTION

Corrosion is a global environmental problem, a lot has been spent on combating corrosion by various countries [1-2]. Corrosion could be in various forms like pitting, crevice etc. Interestingly, corrosion research have not eliminated corrosion totally. Different measures have been put in place to prevent the catastrophic occurrence of corrosion failure which include alloying, sacrificial anode, electroplating, painting and use of inhibitors. Steel is a major material used for infrastructural purposes. API 5L is a mild steel used in the industry for transportation and storage of fluid [3]. API generally are referred to as High strength low alloy steel, having the capacity to withstand flow of fluids at relatively high pressure. Organic inhibitors are used because of their ecofriendly characteristics and accessibility [6, 9]. Different researchers have studied corrosion inhibition of organic materials on different types of materials and environments [2-9]. Their reports showed that organic inhibitors are good corrosion inhibitors. Pawpaw leaf, Mango leaf and Cow dung is an example of organic material. Pawpaw leaf is scientifically known as Carica papaya Linn leaf, It belongs to the Caricaceae family [12]. It is a tree that florish all year round [14]. The leaf has found usefulness more in the traditional cycle for medicinal purposes [11, 13]. Cow dung, also known as cow manure is the waste product of bovine animal species. These species include domestic cattle ("cows"), bison ("buffalo"), and water buffalo. Cow dung is the undigested residue of plant matter which has passed through the animal's gut. The resultant matter from the animal is rich in minerals. Cow dung color ranges from greenish to blackish, often darkening soon after exposure to air. They are often used as manure. Dung could be collected and used to produce biogas to generate electricity and heat. Cow dung is high in organic materials and rich in nutrients. It contains about 3% nitrogen, 2%phosphorus, and 1% potassium. In addition, cow manure contains high levels of ammonia and potentially dangerous pathogens [16-18]. Pawpaw (Papaya) contain a lot of phytochemical properties which includes alkaloids, rutin, and tannins. Loto studied the chemical compositions and structures of pawpaw. He said pawpaw leaf is expected to exhibit electrochemical reactive property and prove effective in corrosion inhibition of steel in the strong nitric acid [5, 15].

Mangoes are juicy fruit from numerous species of tropical trees belonging to the flowering plant genus Mangifera, cultivated mostly for their edible fruit. Mango leaves have high polyphenol content, including xanthonoids, mangiferin and gallic acid (Barreto, 2008). Researches on the cowdung, pawpaw and mango leaves did not study their inhibition capacity on 0.5 M HCl and 0.5 M H_2SO_4. Therefore, this study focus on the use of Pawpaw leaf, Mango leaf and cow dung as inhibitor for corrosion control.

II. MATERIALS AND METHODS

2.1 Materials

API 5L steel was utilized as test material for this research and it was supplied by Advanced Materials and Electrochemical Research Group (AMERG) at the Department of Metallurgical and Materials Engineering. Federal University of Technology, Akure Nigeria. The elemental chemical composition of the steel was determined using a spark spectrometric analyzer. The API 5L steel was cut to dimensions of 10 mm by 10 mm with a thickness of 6 mm for use as test coupons. Each coupon was degreased with ethanol and surface preparation of the coupons were performed by standard procedures of mechanically polishing their surfaces using silicon carbide emery papers of grade 60, 220 and 1200, washed with distilled water and dried at room temperature.

Table I. Composition of API 5L steel

Element	C	Mn	S	Cr	Ni	Cu	As	Fe
Composition (%)	0.0766	0.2980	0.0239	0.0226	0.0167	0.0235	0.0142	Bal.

2.2 Inhibitor preparation

The materials used for study are agro wastes. They include pawpaw leaves, mango leaves and cow dung. The agro wastes were obtained from The Federal University of Technology, Akure, Ondo State, Nigeria. In order to prepare the extract, the agro wastes were obtained in fresh form, cleaned and subjected to drying in an oven until they were sufficiently dried. This was done to make sure that the natural constituent of the agro wastes were preserved. The agro wastes were pulverized using grinding machine to obtain a very fine powder. About 100 g of each pulverized agro wastes were weighed and soaked in 100 ml of ethanol for 72 hours. The mixture was filtered after 72 hours to obtain the filtrates and further subjected to evaporation in order to leave the sample free of the ethanol. Evaporation was carried out in the laboratory by placing the extracts in a heating pan and heating to a temperature of 80^{o}C on an electric heater. The stock obtained were used in preparing different concentrations of the extracts by dissolving 2.0, 4.0 and 6.0% v/v of the extract in 100 ml of 0.5 M HCl and 0.5 M H_2SO_4 respectively.

2.3 Gravimetric Analysis

The convectional gravimetric or weight loss were used. API 5L steel samples measuring 1cm by 1cm were weighed and subsequently immersed in plastic containers containing 100 ml of the test solutions. The solutions consisted of control solutions (the acidic solution without the addition of inhibitors) and the other one were the acidic solutions with addition of inhibitors. The substrates were held in the solutions for a period of 30 days and weight were measured at intervals of 3 days. The weight loss were calcuated. After the duration, the samples were removed from the test media and reweighed. From the weight loss data obtained, the corrosion rates (CR), inhibition efficiency (IE) and surface coverage (Θ) were calculated.

III. RESULTS AND DISCUSSION

1.1 Gravimetric Results

Table II: corrosion parameters obtained from the weight loss measurements of API 5L steel samples in 0.5 M HCl

Inhibitors (extracts)	Concentration (%v/v)	Immersion time (hours)	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate (mmpy)
Pawpaw leaves	0	720	0.8906	0	0.014
	2.0	720	0.1441	84	0.002
	4.0	720	0.5145	42	0.008
	6.0	720	0.1577	82	0.002
Mango leaves	0	720	0.8906	0	0.014
	2.0	720	0.7581	14	0.012
	4.0	720	0.2133	76	0.003
	6.0	720	0.2402	73	0.004
Cow dung	0	720	0.8906	0	0.014
	2.0	720	0.7581	18	0.011
	4.0	720	0.2133	35	0.009
	6.0	720	0.2402	69	0.004

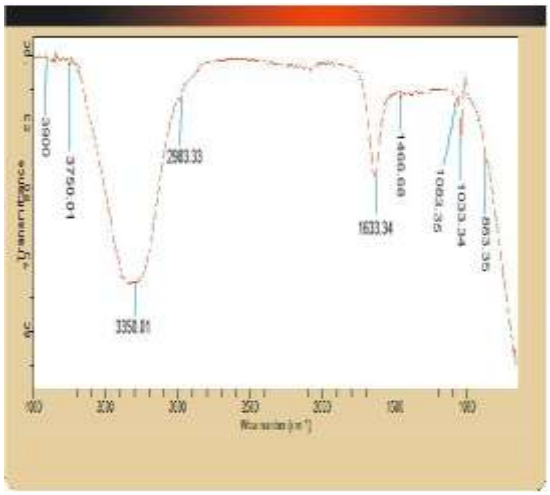
Table III: corrosion parameters obtained from the weight loss measurements of API 5L steel samples in 0.5 M H_2SO_4

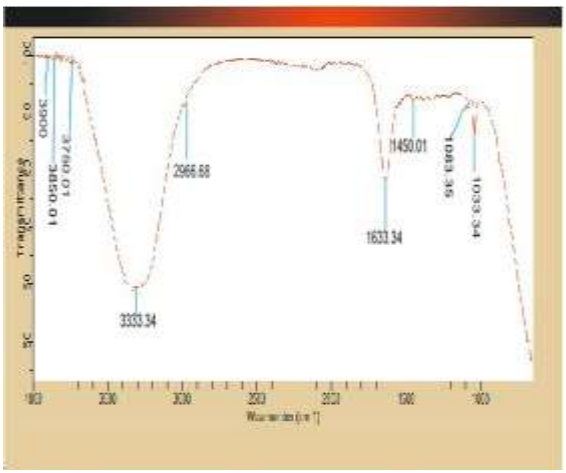
Inhibitors (extracts)	Concentration (%v/v)	Immersion time (hours)	Weight loss (g)	Inhibition efficiency (%)	Corrosion rate (mmpy)
Pawpaw leaves	0	720	2.8987	0	0.045
	2.0	720	2.5274	12	0.039
	4.0	720	2.4392	15	0.034
	6.0	720	2.3454	19	0.033
Mango leaves	0	720	2.8987	0	0.045

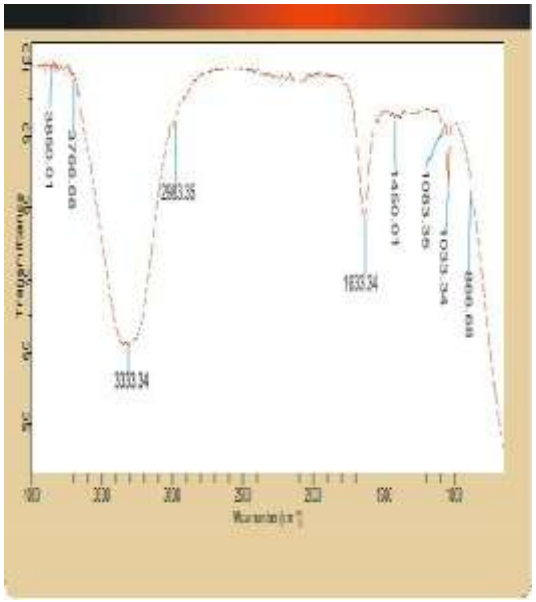
	2.0	720	2.6263	9	0.037
	4.0	720	2.5331	12	0.035
	6.0	720	2.5183	13	0.035
Cow dung	0	720	2.8987	0	0.045
	2.0	720	2.6775	7	0.037
	4.0	720	2.4979	13	0.035
	6.0	720	2.5285	12	0.035

Functional Group Of The Inhibitors

FTIR Fourier Transform infra-red spectroscopy equipment is used to determine the functional groups present in the organic matter to be used as inhibitor. The spectras shows the range of the functional groups present in the inhibitor.







Figures I to III showed the Fourier transform infrared spectroscopy analysis of the extracts. In the analysis of the pawpaw leaf, mango leaf and cowdung, stretching frequencies for the functional group of OH, C=C, C=O, and CN were observed within the range of 3266.68 to 3350.01 cm^{-1}, 1633.34 to 1650.01 cm^{-1}, 1966.8 cm^{-1} and 1033.34 to 1083.35 cm^{-1}. FTIR analysis of the extracts showed the presence of oxygen and nitrogen atoms in functional groups (O-H, C-N) and unsaturated (C=C). The presence of oxygen and nitrogen atoms in the extracts met the general characteristics of typical corrosion inhibitor [10].

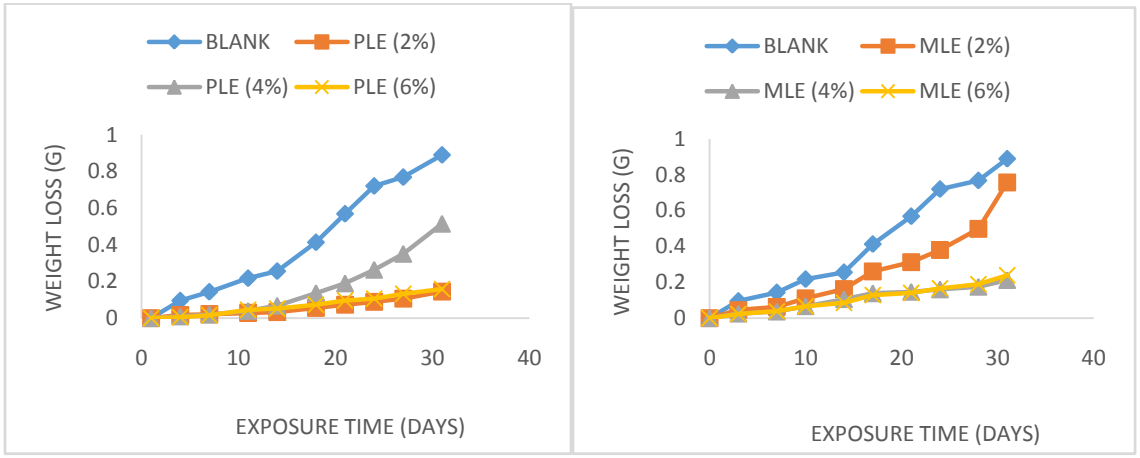


Figure IV: Plot of weight loss as a function of time for corrosion of API 5L steel in 0.5 M HCl in the presence and absence of pawpaw leaves extract.

Figure V: Plot of weight loss as a function of time for corrosion of API 5L steel in 0.5 M HCl in the presence and absence of mango leaves extract.

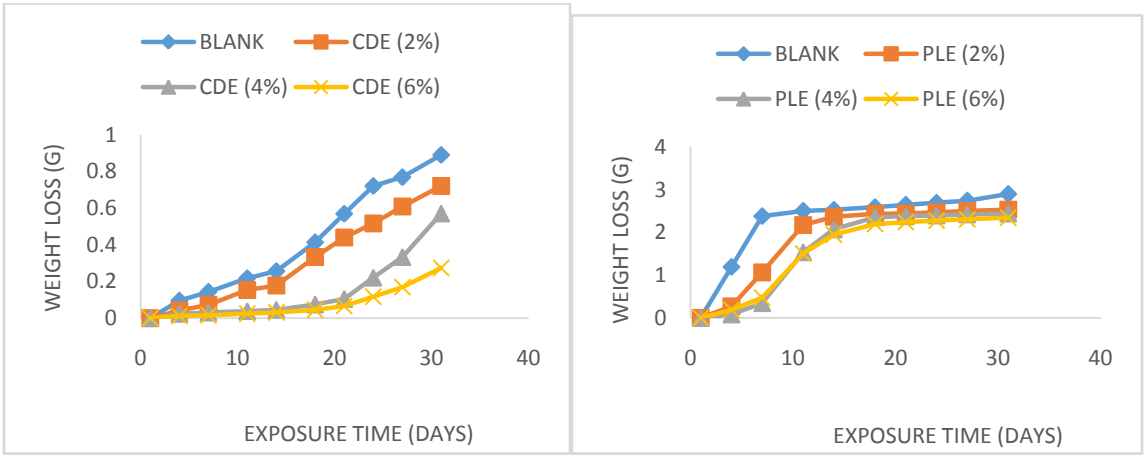


Figure VI: Plot of weight loss as a function of time for corrosion of API 5L steel in 0.5 M HCl in the presence and absence of cow dung extract

Figure VII: Plot of weight loss as a function of time for corrosion of API 5L steel in 0.5 M H_2SO_4 in the presence and absence of pawpaw leaves extract

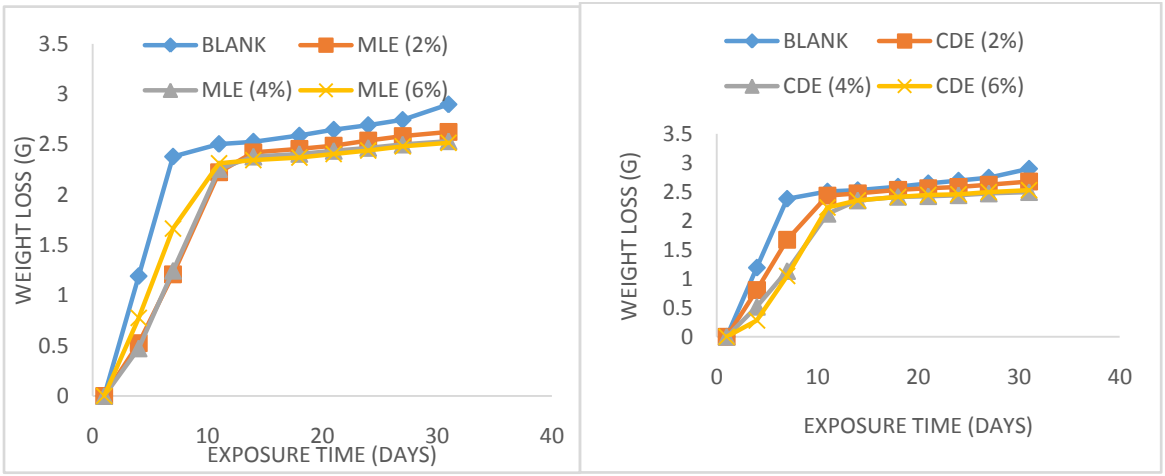


Figure VIII: Plot of weight loss as a function of time for corrosion of API 5L steel in 0.5 M H_2SO_4 in the presence and absence of pawpaw leaves extract.

Figure IX: Plot of weight loss as a function of time for corrosion of API 5L steel in 0.5 M H_2SO_4 in the presence and absence of pawpaw leaves extract.

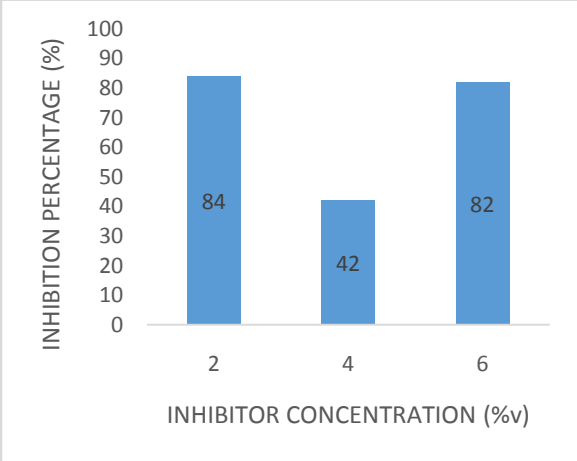


Figure X: Inhibition efficiency of pawpaw leaves extract in 0.5M HCl solution

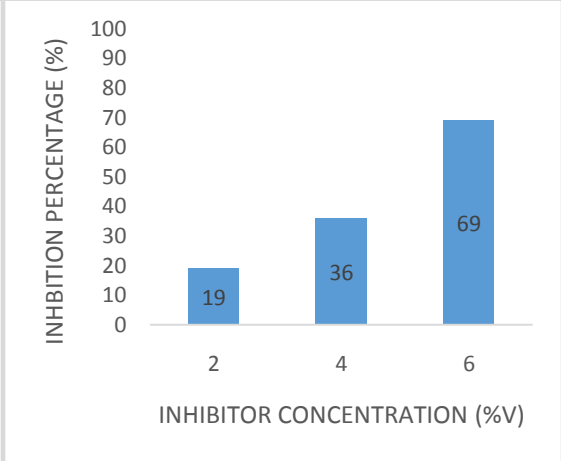
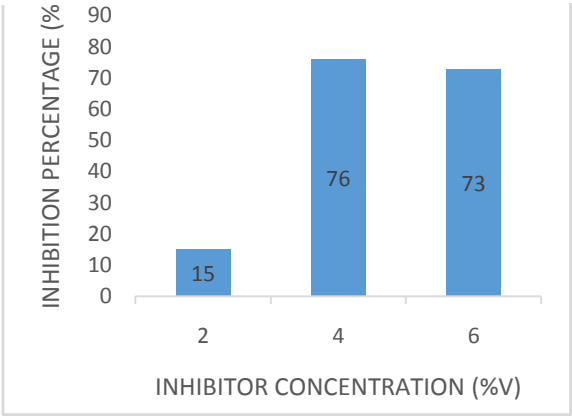


Figure XI: Inhibition efficiency of mango leaves extract in 0.5M HCl solution



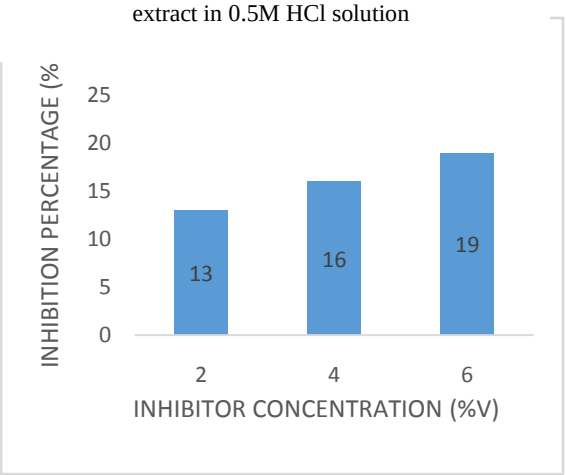
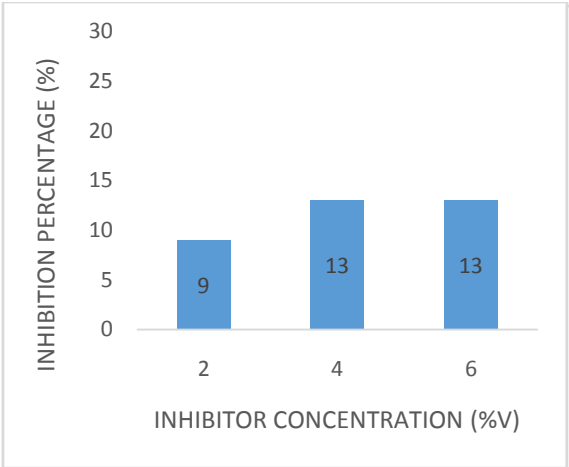


Figure XII: Inhibition efficiency of cow dung extract in 0.5M HCl solution
Figure XIII: Inhibition efficiency of pawpaw leaves extract in 0.5M H_2SO_4



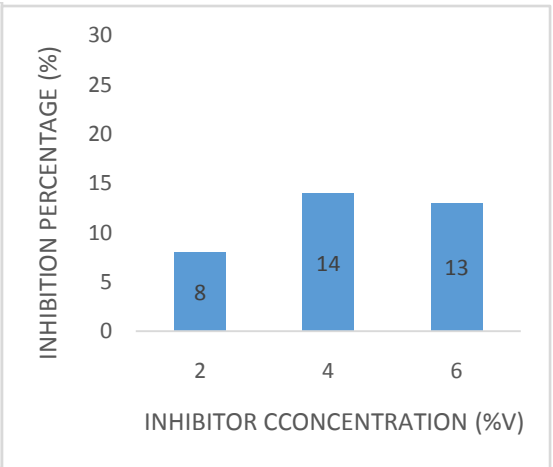


Figure XIV: Inhibition efficiency of mango leaves extract in 0.5M H_2SO_4 solution
Figure XV: Inhibition efficiency of cocoa pod extract in 0.5M H_2SO_4 solution

Figures IV to IX show the variation in mass loss of API 5L steel substrates in 0.5 M HCl and 0.5 M H_2SO_4 in the absence and presence of difference concentration of extract as a function of time.

In figure IV, it was noticed from the plot that weight loss of the sample in blank solution increased with increase in immersion time. Corrosion rate with values of 13.803×10^{-3}, 2.2333

$\times 10^{-3}$, 7.9742×10^{-3} and 2.4442×10^{-3} (mmpy) were obtained at 0.0, 2.0, 4.0, and 6.0 % v/v concentration of the pawpaw leaves extract in 0.5 M HCl solution respectively. Highest inhibition was recorded at 2.0 %v/v concentration of the pawpaw leaves extract with inhibition efficiency of 84 % while least inhibition efficiency was obtained at 4.0 %v/v concentration with inhibition efficiency of 42 %.

Figure V, it was noticed from the plot that weight loss of the sample in blank solution increased with increase in immersion time. Corrosion rate with values of 13.803×10^{-3}, 11.7498×10^{-3}, 3.30592×10^{-3} and 3.7228×10^{-3} (mmpy) were obtained at 0.0, 2.0, 4.0, and 6.0 % v/v concentration of the mango leaves extract in 0.5 M HCl solution respectively. Highest inhibition was recorded at 4.0 %v/v concentration of the mango leaves extract with inhibition efficiency of 76 % while least inhibition efficiency was obtained at 2.0 %v/v concentration with inhibition efficiency of 15 %.

In figure VI, it was noticed that the weight loss and corrosion rate of the blank solution increased exponentially compare to the solution containing the cow dung extracts. Corrosion rate with values of 13.803×10^{-3}, 11.190×10^{-3}, 8.8607×10^{-3} and 4.2374×10^{-3} (mmpy)were obtained at 0, 2, 4, and 6 % v/v concentration of the extract in 0.5 M HCl solution respectively. Furthermore, the inhibition efficiency increased with increase in the concentration of the extract and highest inhibition efficiency was obtained at 6 % v/v with a value of 69 %.

In figure VII, it was noticed from the plot that weight loss of the sample in blank solution increased with increase in immersion time. Corrosion rate with values of 4.4927×10^{-2}, 3.9172×10^{-2}, 3.3921×10^{-2} and 3.2616×10^{-2} (mmpy) were obtained at 0.0, 2.0, 4.0, and 6.0 % v/v concentration of the pawpaw leaves extract in 0.5 M H_2SO_4 respectively. In addition, the inhibition efficiency increased with increase in the concentration of the extract and highest inhibition efficiency was obtained at 6 % v/v with a value of 19 %.

Figure VIII, it was noticed from the plot that weight loss of the sample in blank solution increased with increase in immersion time. Corrosion rate with values of 4.4927×10^{-2}, 3.6523×10^{-2}, 3.5227×10^{-2} and 3.5021×10^{-2} (mmpy) were obtained at 0.0, 2.0, 4.0, and 6.0 % v/v concentration of the mango leaves extract in 0.5 M H_2SO_4 respectively. Furthermore, the inhibition efficiency increased with increase in the concentration of the extract and highest inhibition efficiency was obtained at 6 % v/v with a value of 13 %.

In figure XI, it was noticed that the weight loss and corrosion rate of the blank solution increased exponentially compare to the solution containing the cow dung extracts. Corrosion rate with values of 4.4927×10^{-2}, 3.7235×10^{-2}, 3.4737×10^{-2}, and 3.5163×10^{-2} (mmpy)were obtained at 0, 2, 4, and 6 % v/v concentration of the extract in 0.5 M H_2SO_4 respectively. The highest inhibition efficiency was obtained at 4 % v/v with a value of 14 %.

IV. CONCLUSION

Comparative study of inhibitive properties of pawpaw leaves mango leaves and cow dung extracts on API 5L steel in 0.5 M HCl and 0.5 M H_2SO_4 environments have been studied. The result showed that corrosion rate and inhibition efficiency increased with increased in the concentration of the extracts while in some cases the inhibition efficiency decreased with increased in concentration of extracts. Generally, in both 0.5 M HCl and 0.5 M H_2SO_4 it was observed that weight loss and corrosion rate of the steel samples in blank solutions increased with increase in immersion time. The inhibition efficiencies of the extracts were noticed to be generally higher and more effective in 0.5M HCl environment than 0.5 M sulfuric acid. Highest inhibition efficiency value of 84% was obtained at 2.0% v/v concentration of pawpaw leaves extracts in 0.5 M HCl while highest inhibition efficiency values of 19% was obtained at 6.0% v/v concentrations of pawpaw leaves extract in 0.5 M H_2SO_4 environment. Finally, among the three inhibitors pawpaw leaves extract showed better inhibitive properties in both 0.5 M HCl and 0.5 M H_2SO_4.

ACKNOWLEDGEMENTS

I will like to acknowledge my B.Eng. Students (2017/2018 session) A.O Tiamiyuand A.O Ibrahim for their contributions.

REFERENCE

[1]. S.S. Dara. A textbook of Engineering Chemistry. Chand and company limited. New Delhi, India,1986.

[2]. El-Etre, A.Y. (2006). Khillar extract as inhibitor for acid corrosion of SX 316 steel. Applied surface science vol. 252, pp. 8521-8525.

[3]. L. Xiang-hong, D. Shuduan, X. Xiaoguang and F. Hui. Inhibition effect of bamboo leaves extract on steel and zinc in citric acid solution, Corrosion Sci., 87, p.15-26, (2014).

[4]. I.A. Nnana, B.N. Onwuagba, I.M. Mejeha and K.B. Okeoma. Inhibition effect of some plant extracts on the acid corrosion of aluminum alloy. Africa journal and pure and

applied chemistry, vol. 4(1), pp. 11-16, (2011).
[5]. S. Rajedran, S.V. Ganga, J. Arockiaselvi and A.J. Amalraj. Corrosion inhibition by plant extracts. An overview. Bull. Electrochem. 21: 367-377, (2005).
[6]. J. C. Rocha, P. Gomes, E. D'Elia, A. P. Gil Cruz, L. M. C. Cabral, A. G. Torres and M. V. C.
[7]. Monteiro. Grape Pomace Extracts as Green Corrosion Inhibitors for Carbon Steel in
[8]. Hydrochloric Acid Solutions, Int. J. Electrochem. Sci., 7; 11941 – 11956, (2012).
[9]. A.O. James and O. Akaranta. Inhibitor of corrosion of Zinc in Hydrochloric acid solution by Red onion skin acetone extract, research journal chem. Sci., vol 1, pp. 31-37, (2011).
[10]. A. Singh, E.E. Ebenso and M.A. Quraishi. Corrosion Inhibition of Carbon Steel in Hydrochloric Acid Solution by Some Plant Extract. International Journal of Corrosion, Vol.2012, (2012)
[11]. E.A. Noor. Potential of aqueous extract of Hibiscus Sabdariffa leaves for inhibiting the corrosion of aluminium in alkaline solutions, journal of applied electrochemistry 39(9). pp. 1465-1475, (2009).
[12]. A.F. Gualdron, E.N. Bacerra, D.Y. Pena, J.C. Gutierrrez and H.Q. Bacerra. Inhibitory effect of Eucalyptus and Lippia Alba essential oils on the corrosion of mild steel in hydrochloric acid, J mater Environ Sci 4, 143-158, (2013).
[13]. P. Erasto, D. S. Grierson, and A. J. Afolayan, "Bioactive sesquiterpene lactones from the leaves ofVernonia amygdalina," Journal of Ethnopharmacology, vol. 106, no. 1, pp. 117–120, 2006.
[14]. S. K. Bhattachrjee, "Carica papaya," in Hand Book of Medicinal Plant, S. Jain, Ed., Pointer, Jaipur, India, 3rd edition, 2001.
[15]. M. M. Iwu, "Empirical investigation of dietary plants used in Igbo- Ethnomedicine," in Plants in Indigenous Medicine and Diet, M. M. Iwu, Ed., pp. 131–150, Nina Etkined Redgrove, New York, NY, USA, 1986
[16]. Banerjee A, Vaghasiya R, Shrivastava N, Padh H, Nivsarkar M. Antihyperlipidemic effect of Carica papaya L. in Sprague Dawley rats. Nigerian J. Nat. Prod. Med. 2006; 10: 69-72
[17]. Loto, C. A. Inhibition effect of Tea (Camellia Sinensis) (2011). Extract on the corrosion of mild steel in dilute sulphuric acid, J. Mater. Environ. Sci.; 2 (4) p. 335-344.

O .A. Olaseinde" Comparative Study of Inhibitive Properties of Pawpaw, Mango Leaves and Cowdung on the Corrosion Behaviour of Api 5l Steel In 0.5 M Hcl And 0.5 M H2so4" International Journal of Engineering Research and Applications (IJERA), Vol. 09, No.05, 2019, pp. 28-34