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Corrosion Inhibition Efficiency of Lemon Balm (*Melissa Officinalis*) Leaves Extract on Aluminium in 1 M HCl at Different Temperatures

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Abstract

The inhibitive effect of lemon balm leaves extract on the corrosion of aluminium using weight loss method was investigated. The study was carried out at different concentrations of the extract and temperatures. Inhibition efficiency of 95.57% was obtained. This shows that lemon balm leaves extract could inhibit aluminium corrosion in acidic media to a high degree. The inhibition efficiency of the extract was found to increase as the concentration of the extract increased, but decreased as the temperature increased. The sequence in the relationship between temperature and inhibition efficiency coupled with the Langmuir adsorption isotherm plots supported a physical adsorption mechanism.

1. Introduction

Inhibition efficiency defines the extent in percentage a corroding metal is protected by a certain inhibitor concentration at a particular temperature. High percentage inhibition efficiency translates to effective coverage and protection of the metal in a corroding environment. It depends among other things on the nature of adsorption which in turn depends on structure and functional group of inhibitor molecules, nature of metal involved, the aggressive environment and temperature [1]. Increase in temperature results in decrease in percentage inhibition efficiency in most reactions [2]. Inhibitors of high percentage inhibition efficiency are therefore, being sought for by researchers to effectively minimize the corrosion rate of metals.

Corrosion is a destructive phenomenon which can destroy a metal or alloy through chemical and/or electrochemical reactions of the metal or alloy with the surrounding environment. It is a spontaneous destruction of metals due to heterogeneous chemical reactions [3]. Corrosion prevention and reduction is of high economic importance since most domestic and industrial appliances are made of metals. Therefore, effort is being made to protect these materials through corrosion inhibitors.

To avoid the attack of acid to the bulk metal inhibitors are generally added. Organic compounds containing heteroatoms such as N, O, S etc. are commonly used to reduce the corrosion attack on metals in acidic media. The use of nontoxic inhibitors called green or eco-friendly inhibitors is one of the solutions possible to prevent the corrosion of materials [4].

Corrosion is caused mainly by the presence of acids such as hydrochloric acid (HCl).

Hydrochloric acid is a clear, colourless, highly pungent solution of hydrogen chloride in water. HCl and other acids are used in many industrial processes such as refining of metal, pickling of steel, ($\text{Fe}_2\text{O}_3 + \text{Fe} + 6\text{HCl} \rightarrow 3\text{FeCl}_2 + 3\text{H}_2\text{O}$), metal descaling i.e. removal of calcium carbonate, ($2\text{HCl} + \text{CaCO}_3 \rightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$) etc. The acid when used eventually result in the corrosion of these metals to which it is applied.

Over the years, researchers have come up with different inorganic inhibitors such as chromate, hydrazine, sulphate etc. which are good inhibitors of corrosion but are environmentally hazardous.

The aim of this research therefore, is to seek an inhibitor of high inhibition efficiency without harmful effects to the environment. Thus the use of Lemon balm leaves extract as a natural inhibitor.

Lemon balm is believed to be a good inhibitor because of the chemical composition. It contains eugenol, tannins, terpenes and several other flavonoids, all these compounds are electron rich. Lemon balm also called lemon mint is a native of Europe but also found in abundance in West Africa. It is a lemon-scented perennial shrub with light green leaves which grow up to 70 – 150 cm tall. It was used as incense burnt to ease psychological problems. It was also used as far back as the middle ages to reduce stress and anxiety. It is indeed a plant of great research attraction.

2. Experimental

2.1. Sample Collection

Fresh samples of lemon balm leaves were collected from a farm called Wii-Yorh, in Yorh Beeri, Khana Local Government Area, of Rivers State, Nigeria.

2.2. Preparation of Leave Extract

The leaves were sun dried and grinded into powder, 55.7 g of the leave powder were soaked in 500 cm³ of ethanol. It was stirred and allowed to stand for 7 days. Within the period, the volume of ethanol was constantly checked and more ethanol was added when the ethanol level dropped. The resultant solution was filtered after 7 days. Then more ethanol was added to the leave and allowed to stand for 1 hour for further extraction. After which the solution was filtered again and ethanol was continuously added to the leave extract till the volume of 1,750ml was obtained from which 25 ml, 50 ml, 75 ml, 100 ml and 125 ml were measured and made up to 250 ml mark.

2.3. Preparation of Reagents

2.3.1. Preparation of 1 M HCl

1 M stock solution of hydrochloric acid was prepared by diluting 82.5 ml of the raw acid with distilled water in a 1000 ml volumetric flask and made up to the mark.

2.3.2. Preparation of the Aluminium Coupons

Rectangular specimens of aluminium were cut into dimensions; 4.0cm x 4.0cm x 0.01cm. A perforation of about 2mm in diameter near the upper edge was done to allow passage of rubber thread for suspension of the metal into acid solution. The specimens were cut from the centre of the aluminium sheet and thoroughly cleaned, buffed and rubbed with emery paper to obtain a mirror-like spotless surface. It washed in absolute ethanol, degreased by rinsing in acetone, dried and stored in a desiccator to prevent contact with moisture before use. This method was previously used by other researchers[5]

2.3.3. Weight Loss Determination

The aluminium coupons kept in the desiccator were carefully weighed. Each coupon was placed into a 100ml beaker container containing different concentrations of the inhibitor prepared with 1 M HCl as stated above. The aluminium coupons were placed in the test solution with the aid of rubber thread and was allowed for 30 minutes after which it was retrieved, washed, dried, reweighed, and placed back into the test solution for the next 30 minutes. The experiment was carried out for eight replicate values at the temperature of 30°C and repeated at temperatures of 40°C and 50°C. The temperature was regulated using a thermostatic water bath and the results were recorded and analyzed accordingly.

3. Results and Discussions

The loss in weight (corrosion) of aluminium in 1 M HCl was evident in the gradual reduction in mass of the individual aluminium metal coupons on weighing after retrieval. This was clearly supported by the trend of the graph in Figure 1. The different solutions containing the inhibitor showed tremendous reduction in weight loss against the blank (one without inhibitor). Those with inhibitor appear almost constant compared to the blank which showed a drastic increase in weight loss. This could be attributed to the adsorption of the Lemon balm leaves extract on aluminium surface. Published works had showed similar result [6].

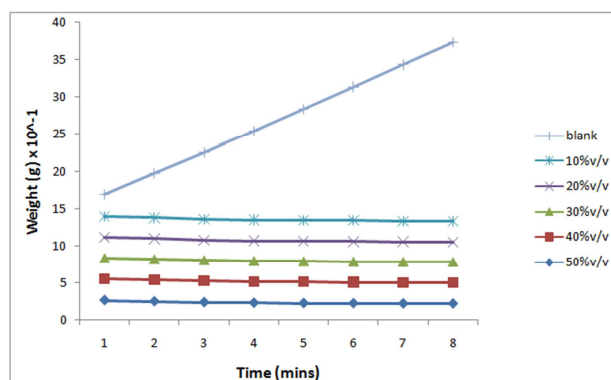


Figure 1. Weight Loss(g) of Aluminium in 1 M HCl with Various Concentrations of Lemon balm extract at 30°C.

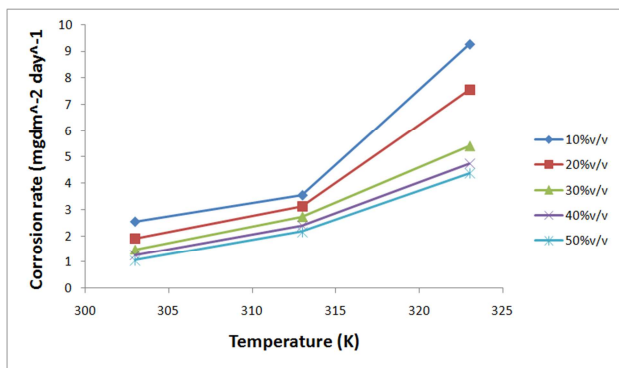


Figure 2. Corrosion Rate against temperature on aluminum in 1 M HCl for Various Concentrations of lemon balm extract.

The rate of corrosion (CR) per day was calculated using;

$$CR = \frac{\Delta W}{Area(cm^2) \times day} \quad (1)$$

Where ΔW is the change in weight loss between the initial and final weight.

The result in Figure 2 shows that the corrosion rate increased with temperature. This result is in agreement with similar investigations previously carried out [7].

While Figure 3 shows that the rate of corrosion decreased with increase in the inhibitor concentration, supporting the effectiveness of the lemon balm leaves extract on minimizing aluminium corrosion in HCl medium.

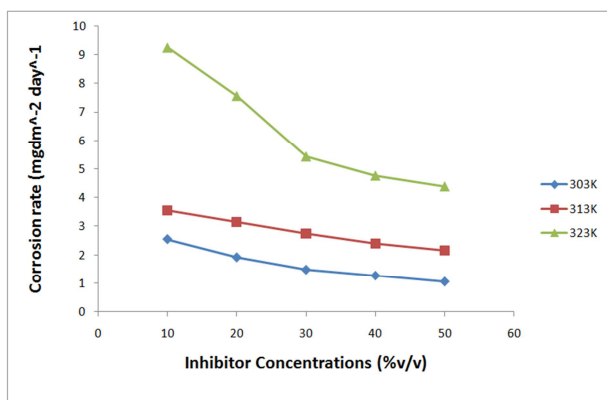


Figure 3. Corrosion Rate against Inhibitor Concentrations on aluminum corrosion in 1 M HCl at different temperatures.

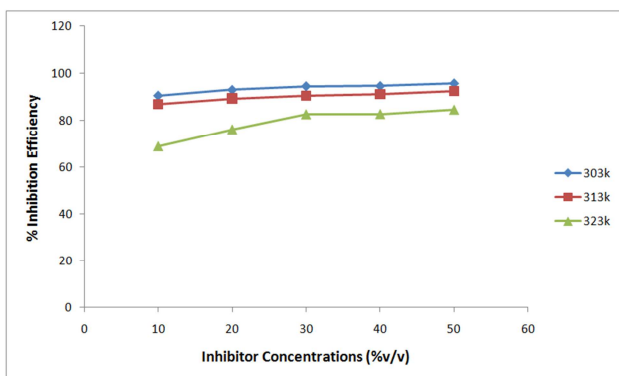


Figure 4. % Inhibition efficiency against Inhibitor Concentrations at various temperatures in 1 M HCl

The percentage inhibition efficiency (I.E) increased with concentration of the inhibitor at all temperatures as shown in Figure 4. I.E increased up to 95% from which further increase in concentration showed little or no effect [8]. The I.E at temperatures 30°C, 40°C and 50°C were calculated using:

$$\% \text{ Inhibition Efficiency} = \frac{\Delta W_b - \Delta W_i}{\Delta W_b} \times 100 \quad (2)$$

Where ΔW_b and ΔW_i are the weight loss data of the metal coupons in the blank and in the solution containing inhibitor respectively [7, 8].

Figure 5 shows that the I.E was adversely affected by increase in temperature [8]. This could be due to the decomposition of the molecules of the inhibitor at that temperature which encouraged desorption.

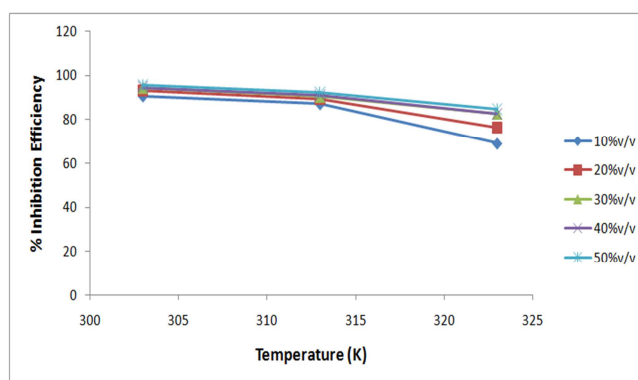


Figure 5. % Inhibition efficiency against temperature at various concentrations of Lemon balm extract in 1 M HCl

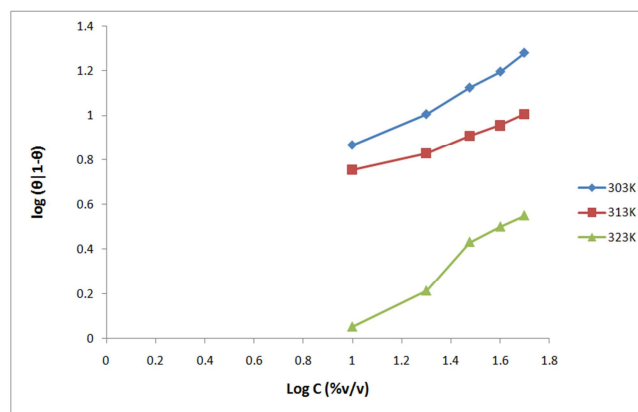


Figure 6. Langmuir adsorption isotherm plot for adsorption of Lemon Balm Extract on aluminium in 1 M HCl medium at different temperatures (°C).

The isotherm studies showed more linearity at low temperature than at high temperature within the studied temperatures of 30°C, 40°C and 50°C as shown in Figure 6 above. This indicates that there was a stronger adsorption at temperature of 30°C (303 K) than that of 50°C (323 K) which showed tendency of desorption. None of the plots has a unity gradient, this is a deviation from Langmuir adsorption isotherm which could be attributed to the interaction of the adsorbed species with each other [9].

Table 1. The Kinetics of Lemon Balm Leaves Extract inhibitor on aluminium corrosion in 1 M HCl solution.

Inhibitor conc.(M)	Rate constant (K)(min ⁻¹)x10 ⁻⁴			Half life (t _{1/2}) (min) x 10 ³			Average activation energy(kJmol ⁻¹)	
	30°C	40°C	50°C	30°C	40°C	50°C	30°C – 40°C	40°C – 50°C
10	9.15	2.29	4.01	757	3026	1728	-113.33	39.76
20	8.36	1.88	3.03	829	3686	2287		
30	6.96	1.63	2.39	996	4251	2900		
40	6.58	1.55	2.31	1053	4471	3000		
50	5.14	1.25	2.06	1348	5544	3364		

The rate constants and the half life (t_{1/2}) for the corrosion of aluminium studied at different temperatures were shown in Table 1 above:

Rate constant (k) at 30°C, 40°C, and 50°C for the reaction was calculated using

$$K = \frac{2.303}{\text{time}} \log \frac{w_i}{w_f} \quad (3)$$

Where w_i and w_f are the initial and final weights of metal coupons.

Half life (t_{1/2}) at 30°C, 40°C, and 50°C was calculated using

$$t_{1/2} = \frac{0.693}{k} \quad (4)$$

Both parameters decreased as temperature increased from 303 K to 323 K. On increasing the concentrations of the studied inhibitor the Rate constant decreased while the half life increased confirming the inhibition of aluminium in 1 M HCl. It is also clear from Table 1 that the average activation energy decreased with increase in temperature which is in line with the general rule for chemical reactions [10].

Table 2. More kinetics of Lemon Balm Leaves Extract inhibitor on aluminium corrosion in 1 M HCl solution.

Concentration	Surface Coverage (θ)			Corrosion rate (mdd)mgdm ⁻² day ⁻¹ x10 ³			Corrosion rate (mm/year)		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
10	0.88	0.85	0.53	2.54	3.54	9.25	25.88	35.64	92.43
20	0.91	0.87	0.62	1.91	3.13	7.56	19.37	32.53	74.81
30	0.93	0.89	0.73	1.48	2.74	5.42	15.92	28.22	57.00
40	0.94	0.90	0.76	1.27	2.39	4.75	13.13	24.38	47.91
50	0.95	0.91	0.78	1.06	2.15	4.37	10.65	22.14	44.98

Surface Coverage (θ) of the Lemon balm leaves extract on aluminium surface was calculated using

$$\theta = \frac{\Delta W_b - \Delta W_i}{\Delta W_b} \quad (5)$$

The surface coverage (θ) as shown in Table 2 increased with concentrations of the lemon balm inhibitor at the various temperatures. This shows that more of the inhibitors are adsorbed on the aluminum surface. It is also clear from the Table 2 above that the corrosion rate decreased with increase in the concentrations of the inhibitor due to the increased coverage which reduced the corrosion site for the corrosive reaction of the acid. This confirmed that the lemon

balm extract inhibits the corrosion of aluminium in 1M HCl at the studied temperatures.

Free Energy of adsorption (ΔG_{ads}) of the reaction was obtained from

$$\Delta G_{ads} = -RT \ln(55.5K_{ads}) \quad (6)$$

The negative free energy of adsorption (ΔG_{ads}) Table 3 implies spontaneous adsorption of the lemon balm leave extract inhibitor on the metal surface [1], while the positive values of both ΔS_{ads} and ΔH_{ads} in Table 4 could be due to displacement of water molecules by the Lemon balmleaves extract inhibitor.

Table 3. Free Energy of Adsorption ΔG_{ads} for corrosion of aluminium in 1M HCl,

Concentration of Inhibitor (%v/v)	Free energy of adsorption ΔG _{ads} (kJmol ⁻¹)			K _{ads} x10 ⁻³		
	30°C	40°C	50°C	30°C	40°C	50°C
10	-16.07	-17.09	-19.42	10.6	12.8	24.9
20	-13.67	-14.98	-17.41	4.1	5.7	11.8
30	-12.10	-13.56	-15.85	2.2	3.3	6.6
40	-10.97	-12.62	-14.88	1.4	2.3	4.6
50	-10.12	-11.67	-14.07	1.0	1.6	3.4

Heat of adsorption (ΔH_{ads})

$$\Delta H_{ads} = \ln K_{ads} RT \quad (7)$$

Where K_{ads} is the coefficient of adsorption at temperature (T).

Entropy of adsorption (ΔS_{ads}) of the reaction system was obtained from;

$$\Delta G^\circ = \Delta H^\circ - T\Delta S \quad (8)$$

$$\Delta S^\circ = \frac{-\Delta G^\circ - \Delta H^\circ}{T} \quad (9)$$

Table 4. The average change in heat of adsorption H_{ads} and entropy of adsorption ΔS_{ads} , of the Lemon balm leaves extract inhibitor in 1 M HCl at different concentrations of the inhibitor.

Concentration of Inhibitor (%v/v)	Heat of adsorption ΔH_{ads} (kJmol^{-1})			Average Energy adsorption ΔS_{ads} (kJmol^{-1}) $\times 10^{-3}$
	30°C	40°C	50°C	
10	-11.45	-11.34	-9.92	90.86
20	-13.85	-13.45	-11.92	90.80
30	-15.42	-14.87	-13.48	90.80
40	-16.55	-15.81	-14.45	90.80
50	-17.53	-16.75	-15.26	90.43

4. Conclusion

The studied lemon balm leaves extract inhibited the corrosion of aluminium in hydrochloric acid medium to a high degree at temperatures of 30°C, 40°C, and 50°C.

References

- [1] Chitra S, Parameswari K, Selvaaj, .Dianiline Schiff Bases as Inhibitors of Mild Steel Corrosion in Acid Media. *International Journal of Electrochemical Science*, 2010; (5): 1675-1697.
- [2] Orubite OK, Jack IR, Ochei M, Akaranta O. Synergistic Effect of Potassium Iodide on corrosion of Mild Steel in HCl Medium by Extracts of Nypa Fruticans Wurmb Extract. *Journal of Applied Science and Environmental Management*, 2007; 11(2): 27-31.
- [3] Suraj BA, Deshpande MN, Kolhatkar DA. Corrosion a Universal Environmental problem: a role of Schiff base metal complexes as Inhibitors. *Journal of Chemical and Pharmaceutical Research*, 2012; 4(2): 1033-1035.
- [4] Hmamou DB, Salghi R, Zarrouk A, Messali M, Zarrok H, Errami M, Hammouti B, BazziLh, Chakir A., Inhibition of Steel Corrosion in Hydrochloric Acid Solution by Chamomile Extract. *Der Pharma Chemica*, 2012; 4(4): 1496-1505.
- [5] James AO, Oforka NC, Olusegun KA, Inhibition of Acid Corrosion of Mild Steel by Pyridoxal and Pyridoxol Hydrochlorides. *International Journal of Electrochemical Science*, 2007; 2(2007): 278-284.
- [6] Toliwal SD, Kalpesh J, PavagadhiT. Inhibition of Corrosion of Mild Steel in 1N HCl Solution by Schiff Base Derived from Non-Traditional Oil. *Journal of Applied Chemical Research*, 2010; 12 (2010) : 24-36.
- [7] Orubite OK, Oforka NC. Corrosion Inhibition of Zinc in HCl using NypaFruticansWurmb Extract and 1,5-Diphenyl Carbazone” *Journal of Applied Science and Environmental Management*, 2004; 8(1):57-61.
- [8] James AO, Akaranta O. The inhibition of Corrosion of Zinc in 2.0M Hydrochloric Acid Solution with Acetone Extract of Red Onion Skin. *African Journal of Pure and Applied Chemistry*, 2009; 3(11): 212- 217.
- [9] Upadhyay RK, Mathur SP. Effect of Schiff Bases as Corrosion Inhibitors of Mild Steel in Sulphuric Acid. *E-Journal of Chemistry*. 2007; 4(3): 408 – 414.
- [10] Anusiem ACI. (2004) Principles of General Chemistry- A Programmed Approach; Revised Edition, Owerri : Great Versatile publishers; 2004