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Full Length Research Paper

Corrosion inhibition of aluminum in 2.0 M hydrochloric acid solution by the acetone extract of red onion skin

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The inhibition efficiency of acetone extract of red onion skin on aluminium in hydrochloric acid solutions has been evaluated by weight loss techniques. Values of inhibition efficiency obtained are dependent upon the concentration of inhibitor and temperature. Generally, inhibition was found to increase with inhibitor concentration, half-life, activation energy but decrease with temperature and first-order rate constant at the temperatures studied. Physical adsorption mechanism has been proposed for the inhibition and Langmuir adsorption isotherm was obeyed. The compound responsible for the inhibitory action of red onion skin is Quercetin. Red onion skin is an inhibitor of aluminium corrosion in 2 M hydrochloric acid solution.

Keywords: Corrosion inhibition, aluminium, weight loss, red onion skin, hydrochloric acid.

INTRODUCTION

The use of inhibitors is one of the best options of protecting metals against corrosion. Several inhibitors in use is either synthesized from cheap raw material or chosen from compounds having heteroatoms in their aromatic or long chain carbon system. However most of these inhibitors are toxic to the environment (Eddy and Ebenso, 2008). In an attempt to find corrosion inhibitors which are environmentally safe and readily available, there has been a growing trend in the use of natural products such as leaves or plant extracts as corrosion inhibitors for metals in acid cleaning process (Orubite and Oforka, 2004).

A lot of works have been reported using economic plants such as *Vernonia Amydalina* (bitter leaf) extracts (Loto, 1998), *Nypa Fruticans* Wurmb leaf extracts (Orubite and Oforka, 2004), *Zenthoxylum alatum* plant (Chauhara and Gunasekara, 2006) and *Telfaria occidentalis* extract (Oguzie, 2005) for the acid corrosion of mild steel. Onions have received considerable attention for their healthful, functional benefits (Augusti, 1996). Phytochemicals in onions include the organosulfur compounds such as cepaenes and thiosulfinates, the large class of flavonoids including Quercetin and Kaempferol (Rhodes et. al., 1996) and pigments such as anthocyanins found in red onions and red wine (Patil et al., 1995). Red onion skin has been analysed and found to contain Quercetin (Odozi et. al., 1984), a conjugated and electron rich compound that may likely inhibit the corrosion of metals. In this study, the inhibitory action of acetone extract of red onion skin on the corrosion of aluminium in 2M hydrochloric acid solution has been investigated at three different temperatures (303, 313 and 323K) using weight loss method.

The inhibitory efficiencies (%E) were calculated from the equation below:

$$\%\,\mathrm{E} = \frac{\Delta W_B - \Delta W_i}{\Delta W_B} \quad x \ \frac{100}{1} \qquad (1)$$

Where; ΔW_B and ΔW_i are the weight loss data of metal coupons in the absence and presence of the additives respectively (Orubite and Oforka, 2004).

EXPERIMENTAL

The weight loss corrosion test method was used for this study.

Material preparation

The commercial aluminium (3SR) sheet of thickness 0.1 cm, used for this study was obtained at the World Bank Engineering Workshop, University of Port-Harcourt, Choba, Port Harcourt. The chemical composition and preparation of the aluminium coupons

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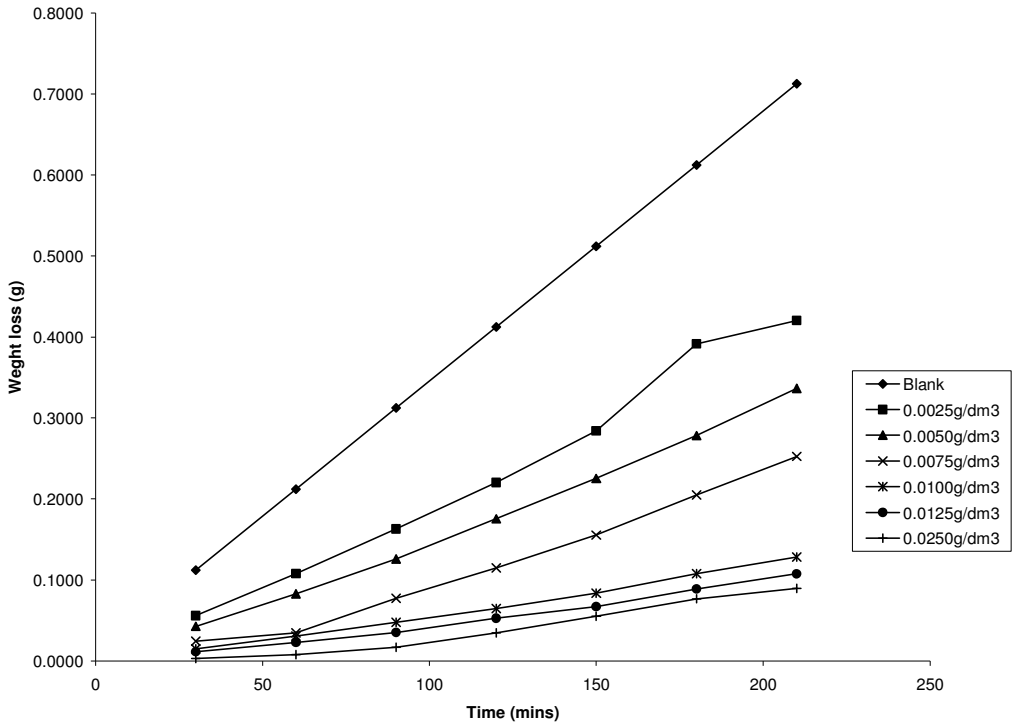

Figure 1. Variation of Weight Loss with Time for aluminium Coupons in 2.0M HCl Solution Containing Different Concentrations of red onion skin extract at 303K.

are described in detail in our previous report (James et. al., 2006). It was mechanically press-cut into 4 × 3 cm coupons. The total geometric surface area of coupon exposed is 24 cm^2.These coupons were used as supplied, without further polishing. However, surface treatment of the coupon involved degreasing in absolute ethanol and drying in acetone (Ita and Edem, 2000). The coupons were then stored in a moisture-free dessicator to avoid contamination before their use in the corrosion studies.

The inhibitor used was acetone extract of red onion skin. The skin of red onion bulb was obtained locally from Choba market, Port-Harcourt. The red onion skin was boiled with 50ml acetone and 50ml water mixture. The resulting red solution was heated to dryness; the powder obtained was then scrapped out and stored in a sample bottle. Six different concentrations (0.0025g/dm^3, 0.0050 g/dm^3, 0.0075g/dm^3, 0.0100g/dm^3, 0.0125g/dm^3 and 0.0250g/dm^3) of the extract were prepared with 2M hydrochloric acid solution and were used for all measurement.

Weight loss measurements

Weight loss study using the red onion skin acetone extract

This work involved the introduction of already prepared concentrations (0.0025, 0.0050, 0.0075, 0.0100, 0.0125 and 0.0250 g/dm^3) of the extract into seven separate beakers maintained at 303, 313 and 323K. The seventh beaker contained only 2.0 M hydrochloric acid solution (without any additive); this was to be used for the blank (control) experiment. Previously weighed coupons were then placed in the test solutions. Each coupon was retrieved from the test solutions at 30 min intervals progressively for 210 min for the experiments at 303, 313 and 323 K. The difference in weight of the coupons was again taken as the weight loss.

RESULTS AND DISCUSSION

Inhibitory action of acetone extract of red onion skin on the corrosion of aluminium

Figures 1, 2 and 3 shows that acetone extract of red onion skin is indeed a corrosion inhibitor for aluminium in hydrochloric acid solution since there was a general decrease in weight loss at the end of the corrosion-monitoring process at the temperatures studied.

From the variation of weight loss with time of exposure of aluminium in 2M hydrochloric acid (blank) at 303 K (Figure 1) compared with those containing the additives, there is a remarkable decrease in weight loss signifying corrosion inhibition.

At 313 K, as the concentration of red onion skin extract increases from 0.0025 to 0.0250 g/dm^3, the weight losses of the aluminium coupons reduce as shown in Figure 2. This shows us that red onion skin extract is still effective in inhibiting the corrosion of aluminium at 313 K. The weight loss of the aluminium coupons still reduced with increasing extract concentration as seen in fig. 3. This depicts that, even at 323K, red onion skin extract inhibits the corrosion of aluminium in hydrochloric acid solution.

Effect of temperature on the inhibtion efficiency of acetone extract of red onion skin

The effect of increase in temperature on the inhibition

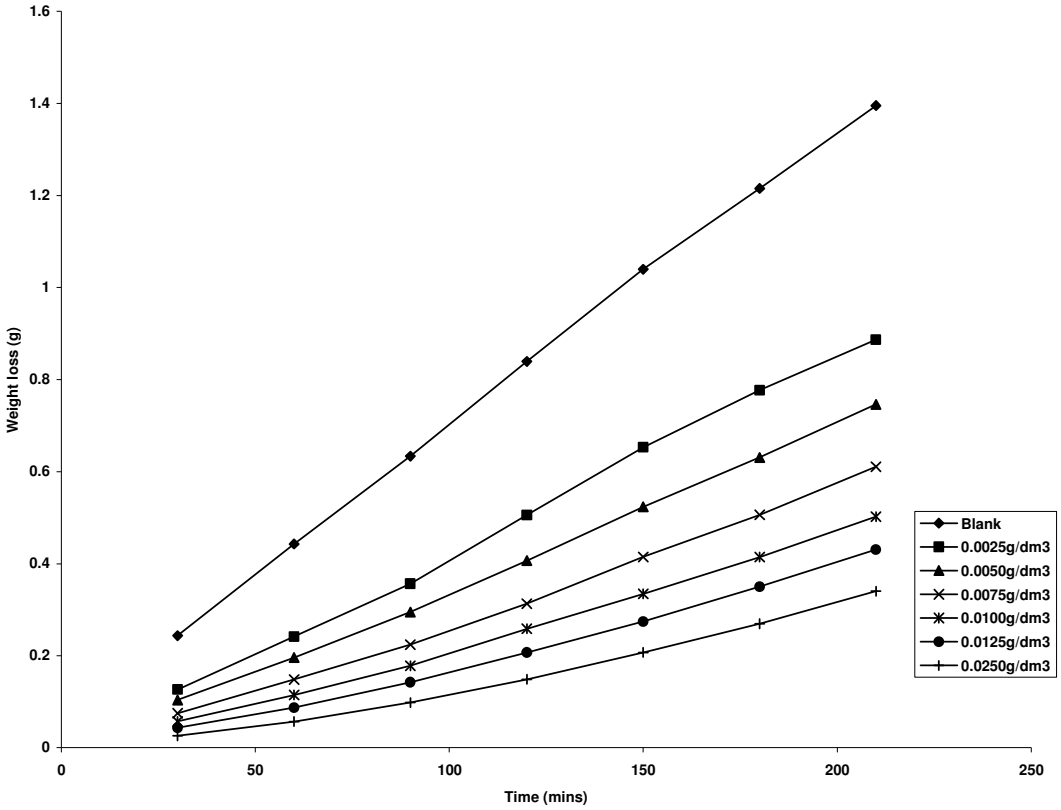

Figure 2. Variation of Weight Loss with Time for aluminium Coupons in 2.0M HCl Solution Containing Different Concentrations of red onion skin extract at 313K.

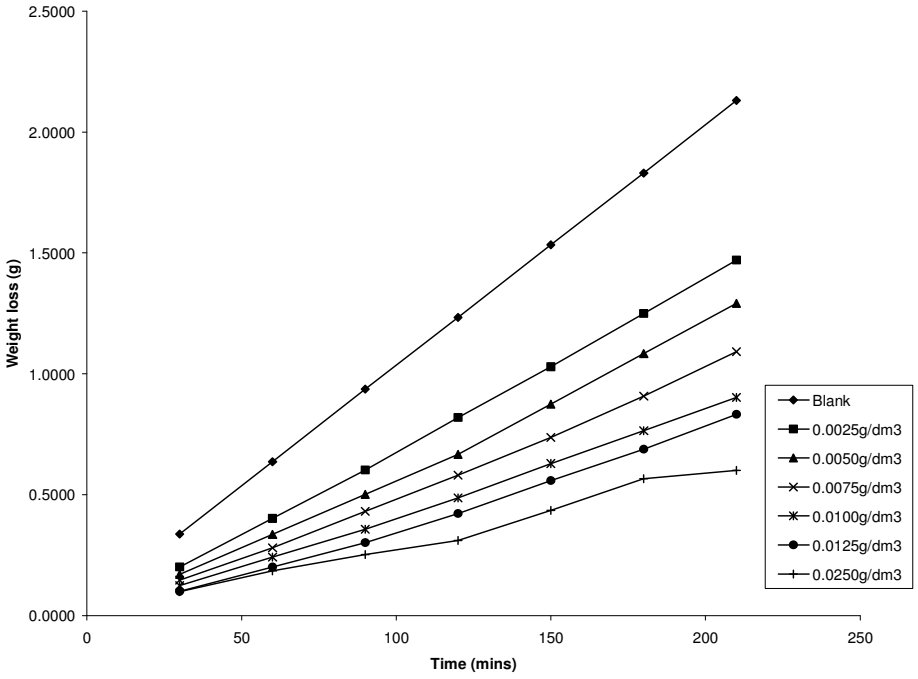

Figure 3. Variation of weight Loss with Time for aluminium Coupons in 2.0 M HCl Solution Containing Different Concentrations of red onion skin extract at 323K.

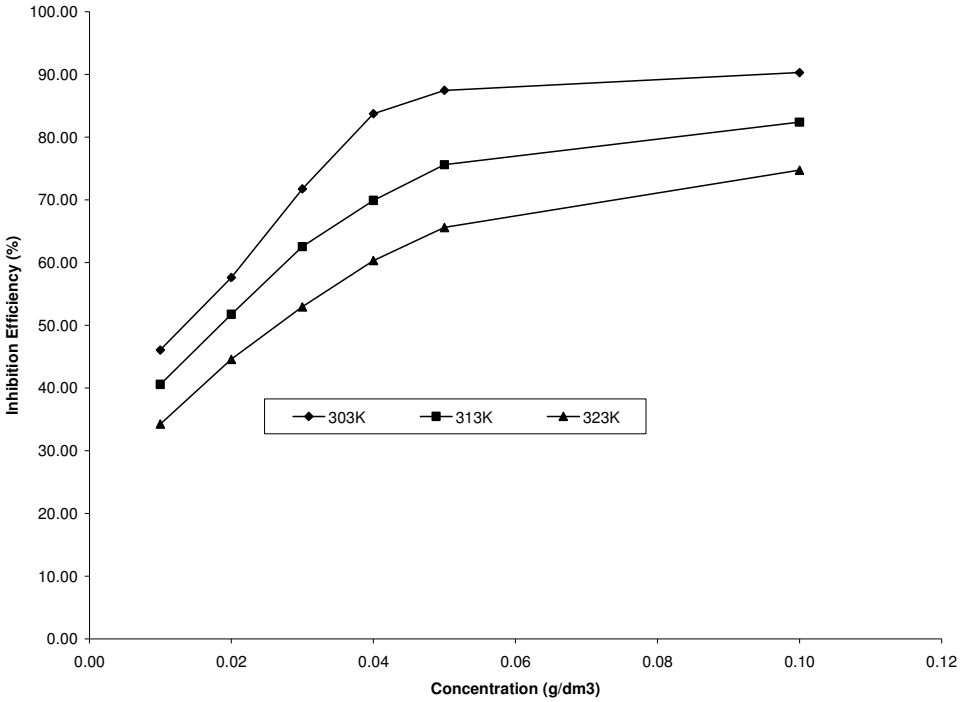

Figure 4. Variation of Inhibition Efficiency with Inhibitor Concentration for aluminium Coupons in 2.0M HCl Solution Containing red onion skin extract at Three Different Temperatures.

efficiency of red onion skin extract is displayed graphically in Figure 4. The immersion time for this Figure is 30 min intervals for 210 min.

We can observe from the graph that, as the reaction temperature is increased from 303 to 313 and to 323 K, the inhibition efficiency decreases. Thus, it is appropriate to say that decreasing temperature favours the inhibition efficiency of red onion skin extract on aluminium in hydrochloric acid.

Effect of concentration increase on the inhibtion efficiency of acetone extract of red onion skin

Figure 4 also portrays an increase in inhibition efficiency of red onion skin extract as the concentration of the extract increases in the acid solution. This can be observed from the upward progression of all three temperatures.

Kinetic treatment of weight loss results

The corrosion reaction is a heterogeneous one, composed of anodic and cathodic reactions with the same or different rate. It is on this basis that kinetic analysis of the data is considered necessary.

In this present study, the initial weight of aluminum coupon at time, t is designated Wi, the weight loss is ΔW and the weight change at time t, (Wi - ΔW). The plots of log (Wi - ΔW) against time (min) at 303 K and other temperatures studied, showed a linear variation which confirms a first order reaction kinetics with respect to the corrosion of aluminium corrosion in 2 M HCl solutions in the presence of the red onion skin extract (Figure 5). The rate constant, half-life time and activation energy were calculated as shown in our earlier report (James et al., 2006). There is a general decrease in the rate constants from 303K - 323K with increasing concentrations of the red onion skin extract (Tables 1 and 2).

The increase in half-life ($t_{1/2}$) shown when the red onion skin extract is present further supports the inhibition of aluminium in 2M HCl by the additives. The increase in half life indicates more protection of the metals by the red onion skin extract. On the basis of the experimentally determined activation energy value (44.08 kJ mol^{-1} at 303 - 313 K), the additive is physically adsorbed on the coupons. Therefore, it is probable that a multilayer protective coverage on the entire aluminium surface was obtained.

Adsorption consideration

The plots of C/θ against C (M) that is linear (Figure 6) shows that red onion skin extract obeys the Langmuir isotherm at the concentration and temperatures studied for the metal. The plots support the assertion that the Mechanism of corrosion inhibition is due to the formation

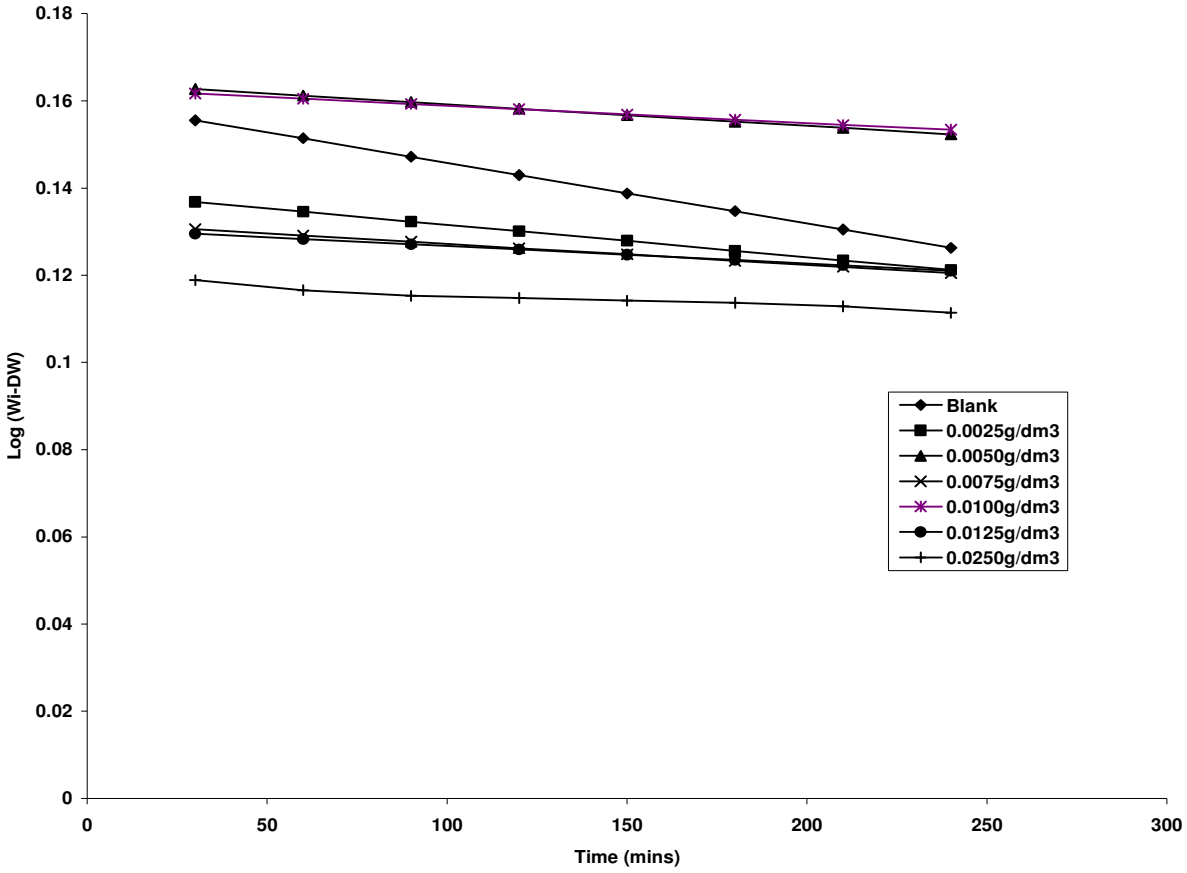

Figure 5. Variation of Log (Wi - ΔW) with time (mins) for aluminium coupons in 2M HCl solution containing red onion skin extract at 303K.

Table 1. Kinetic data for Aluminium in different concentrations of hydrochloric acid solution without additives (Inhibitor).

Hydrochloride acid concentration (M)	Rate Constant, K (day-1) X 10^{-3}			Half-Life, $t_{1/2}$ (days) X 10^{2}			Activation energy $kJmo1^{-1}$	Average activation energy $kJmo1^{-1}$
	303K	313K	323K	303K	323K	323K		
1.0	2.69	3.53	4.48	2.58	1.96	1.55	21.43	
2.0	5.63	6.81	8.88	1.23	1.02	0.78	15.01	
3.0	7.90	10.42	12.94	0.88	0.67	0.54	21.83	20.15
4.0	10.83	14.19	19.35	0.64	0.49	0.36	21.31	
5.0	13.33	17.43	22.05	0.52	0.40	0.31	21.15	

Table 2. Kinetic data for aluminium in 2M HCl containing red onion skin extract from weight loss measurement.

Inhibitor concentration (M)	Rate constant, K (day^{-1}) X 10^{-3}			Half-Life, $t_{1/2}$ (days) X 10^{2}			Activation energy $KJmo1^{-1}$		Average activation energy $KJmo1^{-1}$	
	303K	313K	323K	303K	313K	323K	303K – 313K	313K-323K	303K - 313K	313K -323K
1.0 X 10^{-6}	3.11	4.37	6.96	2.23	1.59	1.00	26.82	39.13		
1.0 X 10^{-5}	2.54	4.31	6.30	2.73	1.61	1.10	41.70	31.91		
1.0 X 10^{-4}	2.09	3.54	5.75	3.32	1.96	1.21	41.56	40.78	44.08	36.85
1.0 X 10^{-3}	1.55	3.03	4.62	4.47	2.29	1.50	52.86	35.46		
1.0 X 10^{-2}	1.10	2.28	3.54	6.30	3.04	1.96	57.48	36.99		

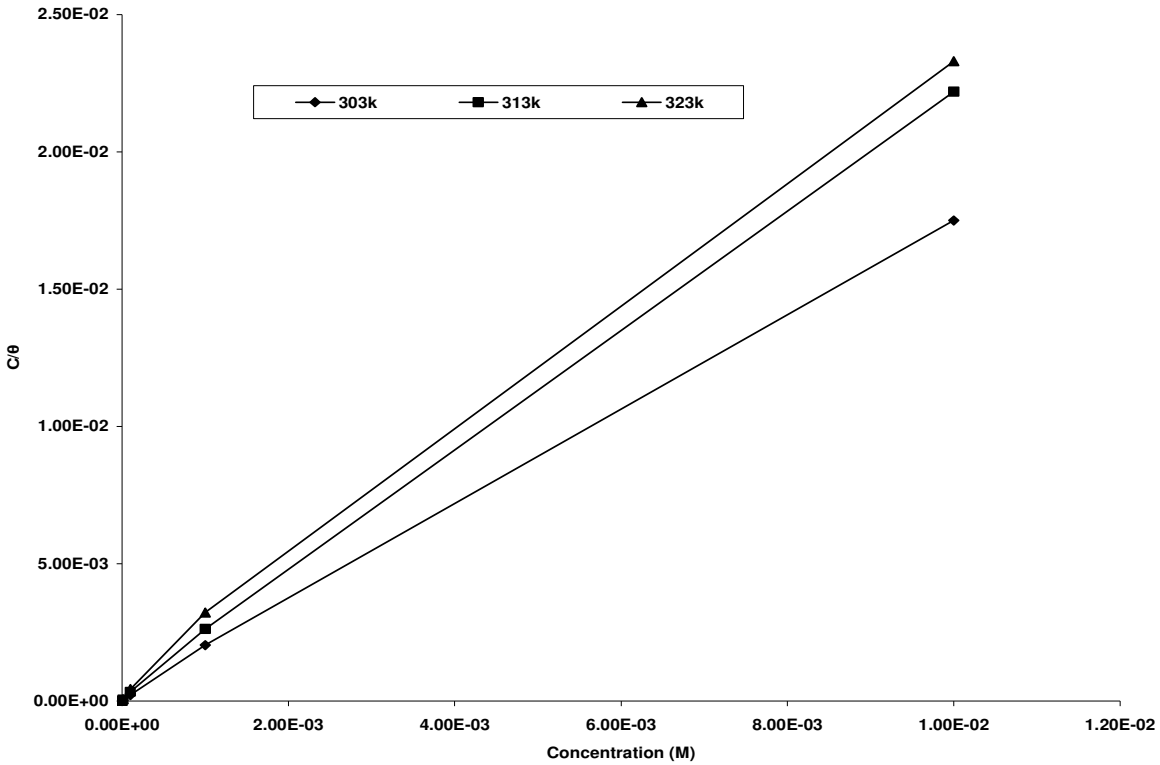

Figure 6. Langmuir adsorption isotherms plotted as C/θ versus C for inhibition of aluminium corrosion in 2M HCl solution by red onion skin extract.

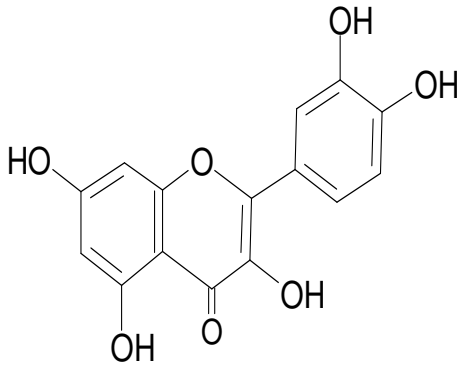

Figure 7. The structure of Quercetin (Red onion skin).

and maintenance of a protective film on the metal surface and that the additive covers both the anodic and cathodic sites through uniform adsorption following Langmuir isotherm.

The inhibitory active component of red onion skin

The inhibitory action of red onion skin was due to the presence of Quercetin (Figure 7). Quercetin is one of the flavonoid compounds present in red onion skin (Rhodes et. al., 1996). It is a compound with conjugated system and contains heteroatoms and carbonyl groups that are electron rich which can serve as a good adsorption site onto the metal surface thereby inhibiting the corrosion of the aluminium.

Conclusion

From the results of this study, the following conclusion can be drawn: (1) Acetone extract of red onion skin is an

effective inhibitor of the corrosion of aluminium in 2 M hydrochloric acid solution at 303, 313 and 323 K; (2) The inhibitor efficiency increase with increased inhibitor concentration and decreased temperature; (3) The oxygen atoms in Quercetin are electron rich and served as a good adsorption site onto the metal surface; they are therefore responsible for the inhibitory action of red onion skin extract on aluminium in 2 M hydrochloric acid; (4) Mechanism of physical adsorption is proposed and a first order type of reaction is obtained from the kinetic treatment of the data; (5) Acetone extract of red onion skin obeys Langmuir adsorption isotherm at all the temperature studied on aluminium in 2 M hydrochloric acid.

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