Inhibition Characteristics of Watermelon Oil on Aluminium in Acids and Saline Water

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Abstract

The response of aluminium specimens immersed in saline water and 1 molar aqueous solution of acetic and sulphuric acids towards corrosion inhibitive actions of oil locally extracted from seeds of watermelon was investigated. Mirror polished aluminium specimens measuring 10-mm diameter by 20-mm length were immersed in batches of plastic beakers containing 50 ml of saline water and acid solutions with watermelon seed oil concentrations by weight of 0.0, 0.5, 1.0, 1.5 and 2.0% as inhibitors. Weight loss method was used to monitor corrosion rate of the specimens over a period of 240 hours. Results showed that reasonable corrosion and inhibition occurred in specimens immersed in solutions of sulphuric and acetic acids while weight losses in specimens immersed in saline water were very minimal and beyond detectable limits of weighing apparatus used. Statistical average reductions of 26, 1.5, 2 and 16% in corrosion rates were achieved, respectively, with the addition of 0.5, 1.0, 1.5 and 2.0% watermelon seed oil for specimens immersed in sulphuric acid, while 49, 6, 28 and 20% reductions were achieved for aluminium in acetic acid solutions. The oil was therefore more inhibitive in acetic than sulphuric acids.

Keywords: Corrosion inhibition, sulphuric acid, acetic acid, saline water, mineral acid.

1. Introduction

Aluminium always finds very regular and diversified uses in domestic appliances, chemical reactions and storage bottles, vessels and containers, buildings, bridges, packaging foils, automobiles, aircrafts, ships and many other engineering contrivances. It is used for variety of applications due to its light weight, very high strength, good thermal and electrical conductivities, good heat and light reflectivity, its non-rusty nature, non-toxicity and attractive appearance (Berke 1989). Despite these great properties of aluminium, aluminium alloys are not perfect materials for engineering applications in all environments as they suffer corrosion caused by chemical interactions with their surroundings (Khandelwal et al. 2010).

Even though aluminium has long been recognized to display passive behaviour in aqueous solutions, with retained exposure it gradually dissolves in aqueous acid solutions with the liberation of hydrogen (Sethi et al. 2007). Mild sulphuric acid was chosen as one of the corrosive environments of interest in this study to represent the family of mineral acids that are very corrosive on metals. It is common in most engineering environments due to direct presence of sulphur or sulphur hydroxide in most liquid and gaseous fluids in commercial, domestic and industrial services.

Mineral acid is easily generated through microbiologically induced activities stimulated by species of bacteria like sulphate reducing bacteria acting as anaerobic organisms that convert sulphur to hydrogen sulphide (H₂S). Aluminium, steel and copper based alloys can be severely corroded by H₂S gas (Loto 2003). Aerobic bacteria thiobacillus oxidise sulphur, sulphides or sulphates to sulphuric acid causing localised pH depression as low as 1 in metal that causes some severe thinning. Thistlethwayte (1972) showed the primary
sources of the acid-forming thiobacillus, concretivorous bacteria and thioxidants that naturally generate acids.

Corrosion protection must, as a necessity, always be provided for in metals and alloys in contact with all environments. Acetic acid was chosen from the organic group of acids as its properties are representative of acids and juices in fruits, vegetables and other organic materials that can corrode metals. Sea water is the most corrosive natural water to metallic components. It is used in industries like shipping, offshore petroleum exploration, power and coastal industrial plants (for cooling), fire-fighting, oil fuel water injection and desalination plants. Corrosion inhibitive characteristics of watermelon seed oil in selected media that are very commonly encountered by aluminium alloys were studied for 240 hours.

Watermelon is a fruit from a plant of vine-like herb that is botanically known as Citrillus lanatus, which is a member of the cucurbitace family (Wikipedia 2012). Watermelon seed oil is also known as Ootanga or Kalahari oil, traced historically to originate from Kalahari Desert of Africa from which it got the name, Kalahari (El-Adewy and Taha 2001). It contains high amount of unsaturated fatty (mostly in the form of linoleic and oleic) acids. It is light and easily absorbed. It doesn’t clog to pores due to the Omega (6 and 9) acids that it contains (Grenera Nutrients 2009). It is non-greasy, penetrating, and quickly absorbed. It has a very stable shelf life.

Ajala (2002) investigated the corrosion inhibition properties of some selected Nigerian vegetable oils and observed that ground nut and sesame seed oil reduced the corrosion of mild steel in 0.5 M HCl. Igwe (1989) also found out that Nigerian soya beans and cotton seed oil stifled the corrosion of mild steel in mineral acid. He then concluded that the metal corrosion rate can be effectively inhibited with selected vegetable oils extracted from local agro-products. Oloruntoba et al. (2011) showed that marine water corrosion on metals can be inhibited with herbal extracts from certain Nigerian vegetables. Toliwal and Jadav (2011) showed that vegetable oils are good corrosion inhibitors because of the hydrazides contained in their fatty acids.

These previous related studies prompted this one to investigate the response of aluminium to corrosion inhibition properties of watermelon seed oil, sea water, sulphuric and acetic acids. This work is aimed at evaluating and comparing the effects of adding watermelon seed oil on the corrosion rate of aluminium immersed in sea water, sulphuric and acetic acids. The objectives are: to expose samples of aluminium alloys obtained from local Nigerian production plant to aqueous media of saline water, molar sulphuric and acetic acids with watermelon seed oil inhibitor of concentration that ranges from 0.0% to 2% weight by weight; to determine specimen weight loss over a period of 240 hours; and to compute and compare the corrosion rates.

2. Materials and Methods

2.1 Materials

The experimental materials include: oil extracted from watermelon seeds, 98% concentrated sulphuric acid purchased from chemical dealer’s shop, locally produced aluminium alloy rods, plastic beakers for the set-up; measuring cylinder, conical flask, retort sand, hack saw, emery papers, distilled water and electrical weighing balance.

Physico-chemical properties of the watermelon seed oil used were analysed at the laboratory of the National Research Institute for Chemical Technology, Zaria, Kaduna State, Nigeria. The analysis showed that the oil was yellowish in color, with a non-irritating odor, oily and non-bitter in taste. Its refractive index was 1.4696 at 25°C, the acid value was 2.8 mg (of KOH/g), the peroxide value was 115 (iodine per 100 g), the iodine value was 1.45 (as oleic acid) and the saponification was 210 mg (of KOH/g). The aluminium alloy used was obtained from and analysed at Kaduna Aluminium Co. Ltd., Kaduna, Kaduna State, Nigeria. The compositional elements are shown in Table 1.
Table 1. Chemical composition of aluminium sample.

<table>
<thead>
<tr>
<th>S/N</th>
<th>Chemical elements present</th>
<th>Composition weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Copper</td>
<td>1.60</td>
</tr>
<tr>
<td>2</td>
<td>Magnesium</td>
<td>2.50</td>
</tr>
<tr>
<td>3</td>
<td>Chromium</td>
<td>0.23</td>
</tr>
<tr>
<td>4</td>
<td>Zinc</td>
<td>5.40</td>
</tr>
<tr>
<td>5</td>
<td>Silicon</td>
<td>0.20</td>
</tr>
<tr>
<td>6</td>
<td>Aluminium</td>
<td>90.07</td>
</tr>
</tbody>
</table>

### 2.2 Methodology

Sample quantities of watermelon seeds were collected through the vendors in different parts of Kaduna, Nigeria, and sun-dried thoroughly. Local extraction method similar to a simple method of extracting oil from groundnut was also used to press and obtain the required quantity of oil from dried watermelon seeds. The obtained quantity of pre-dried watermelon seeds was roasted at elevated temperature and with the aid of a hand press the oil was extracted from the seeds. A molar solution of sulphuric acid was prepared by the following computation. Molecular weight, purity and density of acetic acid were replaced with those of sulphuric acid in the equations below to obtain 1 molar aqueous solution of the acid:

- **Density of** \( \text{H}_2\text{SO}_4 = 1.84 \);  
- **Purity of** \( \text{H}_2\text{SO}_4 = 98\% \); and  
- **Molarity of** \( \text{H}_2\text{SO}_4 = \frac{(\text{Density}\times\text{Purity}\times1,000)}{\text{Molar weight}\times1,000} \),

i.e., \( M = \frac{(1.84\times98\times1,000)}{(98\times100)} = 18.4 \).

Using the relationship \( M_1V_1 = M_2V_2 \), where: \( M_1 = 1; V_1 = 1,000; M_2 = 18.4; \) and \( V_2 = \) unknown, then \( V_2 = M_1V_1 / M_2 \). Thus, 

\[
V_2 = \frac{(1 \times 1,000)}{18.4} = 54.9.
\]

Based on the above calculations, 54.9 ml of concentrated \( \text{H}_2\text{SO}_4 \) was dissolved in 1,000 cm\(^3\) of distilled water to give the needed 1 molar aqueous solution of \( \text{H}_2\text{SO}_4 \). The saline water used was marine water that was sourced from the Atlantic Ocean at Marina, Lagos, Nigeria. It was used as obtained from the ocean. Aluminium specimens measuring 10-mm diameter by 20-mm length were cut out from a 10-mm diameter rod, machined, polished with different grades of sand and emery papers to reveal mirror surfaces.

Polished specimens were degreased with acetone, dried and then stored in desiccators ready for use. Also, 50 ml each of saline water, acetic and sulphuric acid solutions was measured into a plastic beaker and weighed quantities of watermelon seed oil corresponding to 0.0, 0.5, 1.0, 1.5 and 2.0% of weight of each aqueous solution in a beaker was added accordingly. A polished aluminium alloy specimen was then immersed in each beaker as corrosion bath set-up for the research experiment. The beaker with 0.0% oil inhibitor was used as the control experiment to ascertain the corrosion behavior of aluminium in each medium in the absence of the watermelon seed oil.

A weight loss method described by Mattsson (1989) was adapted to measure the corrosion rates of the specimens for the 240 hours of the experiment. Each specimen was removed from a corrosion bath after every 48 hours (2 days), thoroughly cleaned, washed with distilled water, degreased with acetone and weighed with the electronic weigh balance. Differences in weight between present and previous weights were computed and recorded as weight losses for a given period. All the research experiments were conducted under standard room temperature and pressure conditions prevailing in Kaduna, Nigeria.

### 2.3 Computation of Corrosion Rate

The corrosion rate per hour exposure for each specimen immersed in solution was computed from the weight loss obtained from the experiment as described above. Quraishi and Jamal (2000) showed that the corrosion rate \((CR)\) in aqueous solution can be determined using the understated relationship. Based on this, the rate of penetration or material loss of any structural or metallic material can be used to predict the life of that component:

\[
CR = \frac{(K\times W)}{(A\times T\times D)},
\]

where: \( K = \) constant = 87.6; \( W = \) weight loss in grams; \( D = \) density of corroded metal (g); \( A = \) exposed surface area of corroded metal; \( T = \) exposure time (in hours). With the known density of steel (0.0779 g/mm\(^2\)), the corrosion rate was computed.
3. Results and Discussion

The cumulative weight loss in each specimen immersed for 240 hours in aqueous solution of H2SO4 is presented in Fig. 1. Each specimen in solution with 0.0, 0.5, 1.0, 1.5 and 2.0% watermelon seed oil inhibitor showed increased cumulative weight losses with the increase of the exposure time during 0-240 hours. It showed that the H2SO4 solution gradually corroded the aluminium during the exposure period. The corrosion mechanism is based on electrolytic cell formation in which the H2SO4 solution acted as electrolyte and different points in the aluminium specimen with varied electrical potentials acted as tiny anodes and cathodes for a complete galvanic cell circuit. As a result, H2SO4 was ionized into H+ and SO42- in the solution to activate the release of Al3+ at these tiny aluminium anodes. These anions and cations reacted to precipitate aluminium hydroxides, sulphides, sulphates and sulphites with hydrogen bubbles and water that resulted into gradual dissolution and weight loss of specimens. The corrosion here was lower than that of steel in H2SO4 (Al-Turkustani 2010) due to surface protective aluminium oxide that shielded the specimens from the acid attack. The cumulative weight loss in Fig. 1 after 0, 48, 96, 144, 192 and 240 hours of exposure showed a pattern of decreased weight loss with increased inhibitor concentration from 0.0 to 0.5% watermelon seed oil. It increased with increased oil concentration from 0.5% through 1.0 to 1.5% of watermelon seed oil and then decreased with increased inhibitor concentration from 1.5 to 2.0% watermelon seed oil. This pattern is explained by the fact that the increase of watermelon seed oil concentration from 0.5 to 1.5% triggered certain secondary reactions in the corrosion bath that led to additional release and reaction of Al3+ ions and increased weight loss. Above 1.5% watermelon seed oil, this got reduced due to the renewed surface protection of the samples. The inhibition observed in specimens in H2SO4 with watermelon seed oil is due to the presence of unsaturated fatty acids in the watermelon seed oil. Complex fatty acids are chemically stable and are not easily broken down into reactive anions and cathions.

Inhibition of aluminium occurred through a mechanism of watermelon seed oil adsorption onto the metal surface for attack prevention. The intermittent weight losses of aluminium specimens for every 48 hours of immersion in H2SO4 aqueous solution for a total exposure period of 240 hours are as presented in Fig. 2. Except the specimen immersed in solution with 2.0% watermelon seed oil, the other specimens in solutions with 0.0, 0.5, 1.0 and 1.5% watermelon seed oil inhibitor showed a pattern of decreased weight loss with every 48-hour increase in the exposure period during 0-240 hours, that is: 0-48; 48-96; 96-144; 144-192 and 192-240 hours. The experiment showed increased passivity against aluminium with increased time that resulted from the dual process of reduction in hydrogen evolution due to oxide reformation on the metal surface and reduction in the formation of Fe3+ caused by watermelon seed oil adsorbed to the metal surface that shielded it from further corrosive attacks.

![Fig. 1. Cumulative weight loss (mg) of aluminium specimens in H2SO4 for 240 hours.](image1)

![Fig. 2. 48-hour interval weight losses (mg) of aluminium specimens in H2SO4 for 240 hours.](image2)
The watermelon seed oil is rich in Omega 6 and 9 fatty acids (Grenera Nutrients 2009) that are known to impart a good penetrating property to the oil. This assisted the oil adsorption despite the low surface adhesion coefficient of aluminium. The fatty acids adsorbed shielded the metal surface from \( \text{SO}_4^{2-} \) attack and reduced the corrosion.

The corrosion rate of aluminium specimens immersed in \( \text{H}_2\text{SO}_4 \) for 240 hours with watermelon seed oil inhibitor concentrations of 0.0, 0.5, 1.0, 1.5 and 2.0% are presented in Fig. 3. It shows that the metal corrosion rate sharply increased from 0 mg-cm\(^2\)/hr at the beginning of the exposure time to a high value at 48 hours of exposure and thereafter gradually decreased steadily throughout the 240 hours of exposure. The comparison of specimens immersed in \( \text{H}_2\text{SO}_4 \) with no (0.0%) inhibitor to those with watermelon seed oil inhibitor showed that the addition of 0.5, 1.0, 1.5 and 2.0% watermelon seed oil, correspondingly, dropped/raised the corrosion rate: from 454 to 449.95 mg-cm\(^2\)/hr; from 454 to 490.29 mg-cm\(^2\)/hr; from 454.78 to 498.37 mg-cm\(^2\)/hr; and from 454.78 to 421.69 mg-cm\(^2\)/hr after 48 hours. It also dropped: from 155.04 to 94.23 mg-cm\(^2\)/hr; from 155.04 to 138.05 mg-m\(^2\)/hr; from 155.04 to 134.70 mg-cm\(^2\)/hr; and from 155.04 to 116.38 mg-cm\(^2\)/hr after 240 hours, respectively. The experiment implied that average reduction in corrosion rates of 26, 1.5, 2 and 16% occurred, respectively, with the addition of 0.5, 1.0, 1.5 and 2.0% of watermelon seed oil inhibitor within 240 hours of exposure. The corrosion rates followed the similar pattern as observed with cumulative weight loss in Fig. 1 due to similar reasons as adduced above. Figure 4 presents cumulative weight loss in aluminium specimens immersed in acetic acid solutions for 240 hours. Increased weight loss was observed with increased exposure time showing increased corrosive attack of acetic acid on the aluminium specimens. Like what happened to aluminium specimens immersed in \( \text{H}_2\text{SO}_4 \) solutions, electrolytic galvanic cells were set up in corrosion baths with aqueous acetic acid solution acting as electrolyte (with \( \text{H}^+ \) and \( \text{CH}_3\text{COO}^- \) ions) and portions of the aluminium with different electrical potentials acting as tiny localized cathodes and anodes. Weight losses occurred as anodic aluminium was dissolved in the form of \( \text{Al}^{3+} \) ions into the aqueous solution and reacted with \( \text{CH}_3\text{COO}^- \) ions to form aluminium hydroxide precipitate, carbon dioxide, hydrogen and water. The weight losses were due to electrochemical corrosion in the baths. Specimens in solutions with 0.5, 1.0, 1.5 and 2.0% watermelon seed oil inhibitor experienced lower weight loss than that in the solution with no (0.0%) inhibitor due to oil protective film adsorbed onto the metal surface as deduced for Fig. 1. Generally, due to similar reasons the weight loss: decreased with increasing oil concentrations from 0.0 to 0.5%; increased with increased inhibitor concentration from 0.5 to 1.5%; and then decreased with increased oil concentration from 1.5 to 2.0% showing staggered non-consistent pattern as seen in Fig. 4.
The weight loss shown in Fig. 4 was much lower than that observed in Fig. 1 because attacking CH₂COO⁻ ions of acetic acid had longer chains that made it more difficult to access the metal. The ions were less oxidizing than sulphate (SO₄²⁻) ions. Omega 6 and 9 unsaturated fatty acids of watermelon seed oil helped its easy penetration and adsorption onto the aluminium specimen’s surface for protection against reactive ions in aqueous solutions of sulphuric and acetic acids in baths.

Figure 5 shows the interval weight loss after every 48 hours during 0-240 hours for specimens in acetic acid (i.e. weight loss during 0-48; 48-96; 96-144; 144-192; and 192-240 hours). It showed a staggered pattern similar to that in Fig. 4. As it can be observed from Fig. 5, the acid corrosion attack was the worst at the time interval of 48-96 hours when the second reading was taken. The surface oxide and oil protective film that prevented a severe corrosion during the first 48 hours of exposure partially gave way for more acid attacks making it the optimum corrosion period in the experiment.

Computed corrosion rates for samples in aqueous acetic acid solutions during 0-240 hours are shown in Fig. 6. The corrosion rates generally decreased with the increase in exposure time during 0-240 hours. For the observed trend with the inhibitor, the concentration was partially non-consistent. It decreased with increased watermelon seed oil concentration from 0.0 to 0.5%; increased with increased oil inhibitor concentration from 0.5 to 1.5% watermelon seed oil; and decreased with increased inhibitor content of 1.5-2.0% watermelon seed oil. This follows for similar reasons the similar pattern observed in Fig. 1 for the specimens in H₂SO₄.

Comparatively, the addition of 0.5, 1.0, 1.5 and 2.0% watermelon seed oil, correspondingly, decreased the corrosion rate of specimens in solutions without watermelon seed oil inhibitor: from 3.4301 to 2.2018 mg-cm²/hr; from 3.4301 to 3.4301 mg-cm²/hr; from 3.4301 to 2.6230 mg-cm²/hr; and from 3.4301 to 1.4124 mg-cm²/hr after 48 hours of exposure. It dropped: from 2.7441 to 0.9281 mg-cm²/hr; from 2.7441 to 2.3002 mg-cm²/hr; from 2.7441 to 2.1791 mg-cm²/hr; and from 2.7441 to 2.6230 mg-cm²/hr after 240 hours of exposure, respectively.

Statistically based on the above values, watermelon seed oil concentrations of 0.5, 1.0, 1.5 and 2.0% added to acetic acid solution reduced the corrosion of aluminium by 49, 6, 28 and 20%, respectively, within the 240-hour period. Comparatively, Fig. 2 shows that the watermelon seed oil effected a better inhibition on aluminium alloys in acetic acid than in H₂SO₄ solution. The reason for this is as explained above.

![Fig. 5. 48-hour interval weight losses (mg) of aluminium in acetic acid from 240 hours.](image)

![Fig. 6. Corrosion rate (in mg-cm²/hour) of aluminium specimens in acetic acid for 240 hours.](image)

The cumulative weight loss shown in Fig. 7 is for aluminium specimens immersed in saline (sea) water for 240 hours. The weight loss for all the specimens with and without watermelon seed oil inhibitor was flat on the axis showing that no detectable change in
weight occurred. This is due to the high affinity of aluminium for oxygen which quickly reacts with it to form chemically stable surface oxide. Aluminium oxides are known to be very resistant against chemical attacks even in aqueous solutions, particularly if the ions in the solutions are not strong enough to reduce the oxides. The undetected weight loss showed that the Na⁺, CL⁻ and other ions present in the saline water could not cause enough corrosive wear to show a reasonable weight change that the electronic weigh scale could indicate within the exposure time of 240 hours. The intermittent weight loss presented in Fig. 8 and the corrosion rate in Fig. 9 gave a result being flat on the axis similarly to the weight loss in Fig. 7 showing that with or without inhibitor, the saline water used in the study had no deleterious effect on the samples within the period of study. Comparatively, based on the oxidizing strength of the ions present in the aqueous solution in which aluminium was immersed, the sulphuric acid most severely corroded the specimens, followed by the acetic acid and then the saline water which caused some minimal undetected corrosion on the specimens.

4. Conclusion

The foregoing results showed that the watermelon seed oil is a good corrosion inhibitor for aluminium in aqueous solutions of sulphuric and acetic acids. It functions by the dual mechanisms of prevention of hydrogen formation and surface adsorption of the oil for anodic protection of the metal surface against ionization. The saline (sea) water caused minimal corrosion that wasn’t detectable by the measuring apparatus. Therefore, no inhibitive protection was needed by the aluminium alloy as its corrosion was quite negligible in it within the study period. The oil gave better protection to aluminium in acetic than in sulphuric acid.

5. Acknowledgement

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6. References


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