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Gluconates as Corrosion Inhibitor of Aluminum in Various Corrosive Media

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Abstract

Corrosion processes are responsible for huge losses in industry. Though organic, inorganic and mixed material inhibitors were used for a long time to combat corrosion, the environmental toxicity of organic corrosion inhibitors has prompted the search for inorganic corrosion inhibitors. The effect of gluconates as novel corrosion inhibitors on the corrosion of aluminum alloy in acidic and saline media was investigated by electrochemical and weight loss techniques. The effect of inhibitor concentration was also investigated. High resolution scanning electron microscopy equipped with energy dispersive spectroscopy (HR-SEM/EDS) was used to characterize the surface morphology of the metal before and after corrosion. Experimental results revealed that gluconates in the studied solution decreased the corrosion rate at the different concentrations studied. The experimental results obtained from potentiodynamic polarization method showed that the presence of the gluconates in 3.5% NaCl and 0.5 M H₂SO₄ solutions decreases the corrosion current densities (*i*_{corr}) and corrosion rates (CR), and increases the polarization resistance (*R*_p). It was observed that the inhibitor efficiency depends on the corrosive media, concentration of the inhibitor and the substrate material. The adsorption characteristics of the gluconates were also described. Good correlation exists between the results obtained from both methods.

Keywords: aluminum alloy, corrosion, inhibition, gluconates, potentiodynamic polarization, weight loss, SEM/EDS

1. Introduction

1.1. Aluminum alloy

Aluminum compounds occur in aluminum types of clay, but the most useful ore for producing pure aluminum is bauxite. It consists of 45.60% aluminum oxide, along with various

impurities such as iron, sand and other metals [1]. Aluminum is durable, relatively soft, light weight, malleable and ductile metal with physical appearance ranging from silvery to dull gray depending on the roughness of the surface. Aluminum has almost one – third of the stiffness and density of steel. It is easily drawn, machined, cast and extruded. Aluminum is also a good electrical and thermal conductor. Aluminum and its alloys are very important material because of their wide use in many industries. They are used in the aviation, aerospace and automotive industries, in the production of military hardware, in ship building and household appliances [2–4]. Their usefulness is derived from their very good mechanical and physical properties such as their weight-to-high strength ratio, good machining properties, recyclability, and their outstanding corrosion resistance. The corrosion resistance of aluminum and its alloys is attributed to the formation of a stable protective thin film of aluminum oxide when exposed to the atmosphere. Aluminum alloys are therefore used widely as materials for electricity cables, bottle tops, food and beverage containers, and roofing sheets [5]. Despite the huge benefit of aluminum when compared to other metals, it is not always resistant to corrosion completely. When the environment is highly basic or acidic, the protective layer breakdown can occur and its instant renewal may not be fast enough to prevent corrosion [6–9]. Corrosion of aluminum leads to passivation of active cathode material, the electrical resistance of the solid product is increased and the electrolyte is contaminated by its soluble products and increases the self-discharge rate. In efforts to reduce aluminum corrosion, the main approach is to separate the aluminum metal from corrosive environments and this can be accomplished by means of corrosion inhibitors. Therefore, the ability of aluminum to resist corrosion attack in various environments is inadequate and a continuous search for methods for controlling this behavior remains important in the field of corrosion control.

1.2. Corrosion of metals

The corrosion of metals is a serious problem in most industries. Corrosion phenomena, control and prevention are unavoidable major scientific issues that must be addressed daily as far as there are increasing needs of metallic materials in all facets of technological development [10]. Technological progresses require the use of materials in aggressive environments, such as corrosive atmospheres [11]. Corrosion is a degradation of metal due to environmental reactions dissolution; it is an electrochemical process and usually begins at the surface [12, 13]. As a result of daily encounters with corrosion problems such as; waste of valuable resources, costly maintenance, plant shutdowns, expensive overdesign, loss or contamination of products and reduction in efficiency; technological developments are impeded and safety endangered [14, 15]. The multifacet aspect of corrosion problems coupled with responsibilities associated with them only increase the complexity of the subject [16, 17]. This problem has caused the stimulation of many corrosion control research in various oil production facilities around the world [18]. The cost due to corrosion does not only increase rapidly, the quality of the products and the efficiency of the plants is also reduced. In the United States this amount to over 276 billion USD per year. The highest segments of the cost of corrosion are associated with utilities, transportation and infrastructure. Millions of dollars are lost each year because of corrosion including the cost of prevention and maintenance. NACE studies recently estimates global cost of corrosion at \$2.5 trillion annually at CORROSION 2016 conference held

at Vancouver, B.C., which examined the economics of corrosion and the role of corrosion management in establishing industry best practices [19]. Corrosion can be localized by forming a crack or pit, or expand across a wide area by uniformly corroding the surface [20]. Pitting corrosion takes place in materials with surface films protection like corrosion products, the metal exposed releases electrons easily and tiny pits is initiated by the reactions [21]. Galvanic corrosion usually occurs on the surface of metal which have more than one phase, in other for local cells to be set up on heterogeneous surface with different potentials. The preferential attack of grain boundaries without substantial attack of the grains themselves is called intergranular corrosion; it is often caused by the precipitation of fine intermetallics at grain boundaries [22]. Localized corrosion may possibly result in structure failure of metallic materials if it is allowed to reach critical levels [23]. Corrosion resistance of alloys has become a continuous research due to its severe consequences [24]. One of the most useful techniques in protecting and controlling metals against corrosion is the use of inhibitors, especially in saline and acidic media.

2. Corrosion control and monitoring

The practice carried out to assess and predict the corrosion behavior in equipment and operational plant is known as corrosion monitoring. The objectives of corrosion monitoring are:

- To provide information based on the operational state of the equipment with the intent of avoiding unplanned shut-downs occurring from unforeseen deterioration of the plant.
- To provide information on the operating variables and interrelation between corrosion processes to allow more efficient use of the plant.
- To provide information that can be used to prevent potential disasters and safety failures by plant inspection departments.
- To assess process fluids contamination levels.

The principle behind corrosion protection is to influence the reactions which occur during corrosion, it being possible to control the corrosive agent and the package contents, and also the reaction itself in such a manner that corrosion is minimized. Corrosion protection is subdivided into three subtopics: passive, permanent and temporary corrosion protection.

2.1. Passive corrosion protection

Damage is prevented in passive corrosion protection by mechanically isolating the package contents from the aggressive corrosive agents, for example by using films or other coatings and protective layers. This type of corrosion protection changes neither the aggressiveness of the corrosive agent nor the general ability of the package contents to corrode; this is why this approach is known as passive corrosion protection. Corrosion may occur within a very short time if the protective film or layer is destroyed at any point in time.

2.2. Anti-corrosion coating protection

The main purpose of permanent corrosion protection methods is to provide protection at the place of use. Machines are usually located in factory sheds and are protected from extreme variations in temperature, which frequently causes condensation. The stresses presented by biotic, chemical and climatic factors are relatively slight in this situation. Examples of permanent corrosion protection methods are: galvanization, tin plating, copper plating, coating and enameling.

2.3. Temporary corrosion protection

The stresses occurring during handling, storage and transport are greater than those that occur at the place of use. Stresses manifested are; extreme variations in temperature, which result in a risk of condensation. In maritime transport, the elevated salt content of the air and water in the sea salt aerosols may cause damage, due to the strongly corrosion-promoting action of salts. The main temporary corrosion protection methods are as follows: desiccant method, protective coating method and corrosion Inhibitor methods.

Corrosion scientists are relentless in search of more and better efficient and cheap ways of mitigating the corrosion of metals and alloys. One of the ways of combating corrosion is the addition of inhibitors to the corroding environment. The various types of inhibitors can be classified as organic and inorganic. Corrosion inhibitors are used widely in industries to reduce or prevent corrosion rate of metals in acidic, alkaline media, and industrial processes such as acid descaling, acid pickling and cleaning of refinery equipment and oil well acidizing.

3. Corrosion inhibitors

Certain substances which, when added to a corrosive system, modify the surface of the material to reduce the corrosion rate, are called inhibitors [25]. The use of chemical inhibitors to mitigate the rate of corrosion is quite varied. In the processing industries and oil extraction, inhibitors have always been considered to be one of the first ways against corrosion. Corrosion inhibitor performance has historically been described by two concepts namely: corrosion inhibitor availability and corrosion inhibitor efficiency. This essentially examines the ratio of the uninhibited and inhibited corrosion rates, and expresses this as a percentage. An inhibitor that reduced corrosion rates by a factor of 10 would be 90% efficient. This leads to the development of the concept of “availability of corrosion inhibitor.” In this concept, performance is determined based on the summation of total metal loss over a period of time, assuming periods of uninhibited corrosion and inhibited corrosion. Corrosion availability concept is currently replacing the inhibitor efficiency concept with respect to use in corrosion inhibition concepts for systems design [26]. A great number of scientific researchers have responded to this need and it has generated increased research studies into the use of inhibitors. Compounds containing nitrogen as corrosion inhibitors have been investigated thoroughly by many authors; imidazole and benzimidazole derivatives [27–29], bipyrazole [30], quaternary ammonium salts [31], substituted aniline-N-salicylidenes [32], cationic surfactants [33], phosphorous containing

inhibitors [34, 35]. The research on corrosion inhibition of aluminum alloy is ongoing due to this fact our research work focuses on the effectiveness of gluconates as corrosion inhibitors for aluminum alloy in 0.5 M H_2SO_4 and 3.5% NaCl solutions. Attempt at making novel contribution to this growing research area has necessitated the present investigation. Weight loss and potentiodynamic polarization techniques were used to examine the rate of deterioration. The effect of zinc gluconate and ferrous gluconate on the aluminum alloy surface in the test media was studied using high resolution scanning electron microscope equipped with energy dispersive spectroscopy (HR-SEM/EDS). Studies on surface characterization, adsorption mechanisms and electrochemical analysis of corroded materials were also carried out.

3.1. Industrial applications of corrosion inhibitors

3.1.1. Petroleum production

Petrochemical and refineries industries use different film-forming inhibitors to control wet corrosion. Water-soluble and water-soluble-oil-dispersible type inhibitors are continuously injected or oil-soluble and oil-soluble-water-dispersible type inhibitors are intermittently applied to control corrosion.

3.1.2. Internal corrosion of steel pipelines

Gathering pipelines, operating between oil and gas wells and processing plants, have corrosion problems similar to those in refineries and petrochemical plants. The flow regimes of multiphase fluids in pipelines influence the corrosion rate. At high flow rates, flow-induced corrosion and erosion-corrosion may occur, whereas at low flow rates, pitting corrosion is more common. Internal corrosion of pipelines is controlled by cleaning the pipeline and by adding continuous and/or batch inhibitors.

3.1.3. Water

Potable water is frequently saturated with dissolved oxygen and is corrosive unless a protective film, or deposit, is formed. Cathodic inhibitors, such as calcium carbonate, silicates, polyphosphates, and zinc salts, are used to control potable water corrosion. Water is used in the cooling system in many industries.

3.1.4. Acids

Acids are broadly used in pickling, cleaning of oil refinery equipment, heat exchangers and in oil well acidizing. Mixed inhibitors are widely used to control acid corrosion.

3.1.5. Automobile

Inhibitors are used in an automobile for two reasons which are; to reduce the corrosivity of fluid systems (internal corrosion), and to protect the metal surfaces exposed to the atmosphere (external corrosion). Internal corrosion is influenced by the coolants, flow, aeration, temperature, pressure, water impurities, corrosion products, operating conditions and maintenance of the system.

3.1.6. Paints

Finely divided inhibiting pigments are frequently incorporated in primers. These polar compounds displace water and orient themselves in such a way that the hydrophobic ends face the environment, thereby augmenting the bonding of the coatings on the surface.

4. Corrosion prevention of aluminum alloy

Gluconic acids are environmentally suitable non-toxic compounds. It is abundant in plants, fruits and other foodstuffs. Gluconic acid and its derivatives are used in the formulation of pharmaceuticals, foods, and cosmetics as mineral supplements to prevent the deficiency and as buffer salts. They are also used as ingredients in various hygienic products. In industrial applications, they are used for scale removal in metal cleanings, industrial and household cleaning compounds including mouth washer, metal finishing, water treatments, and as paper and textile auxiliaries. For these reasons, it is very useful to study the corrosion behavior of aluminum alloy in acidic and saline media using gluconates as inhibitor. Gluconate is a large hydrocarbon oxyanion [36], aluminum would be expected to anodize in the presence of this kind of ion. The aim of this research was to evaluate the effect of ferrous gluconate and zinc gluconate concentration on corrosion of aluminum alloy in different environments and to estimate optimal concentrations of ferrous gluconate and zinc gluconate required for satisfactory inhibition. Diverse researches carried out by different authors regarding the improvement of aluminum alloy using different inhibitors in various media have been attempted by different authors. Popoola et al. [37] confirm that in aggressive environment, the protective film on the surface of aluminum usually breakdown leading to initiation and further propagation of pits. The authors studied the corrosion inhibition of aluminum alloy in 2 M HCl and HNO₃ with *Arachis hypogaea* natural oil as an inhibitor using potentiodynamic polarization and gravimetric techniques at 25°C. The obtained results showed that *Arachis hypogaea* oil in 2 M HCl and HNO₃-solutions decreased the corrosion rate of aluminum alloy at different concentrations of inhibitor considered. Umoren and Solomon [38] researched on the influence of bromide and iodide ions on the inhibitive effect of polyacrylamide (PA) on aluminum corrosion in HCl solution show that the halide additives synergistically increased the inhibition efficiency of polyacrylamide and the increase in inhibition efficiency was found to be more obvious in iodide than bromide ions. Obot and Obi-Egbedi [39] confirmed fluconazole (FLC) as a corrosion inhibitor for aluminum in hydrochloric acid solution. Garcia et al. [40] worked on the effect of solution pH on the anti-corrosion performance of different inhibitors K₂Cr₂O₇, CeCl₃, and Ce(dbp)₃ on aluminum alloy (AA2024-T3) using the multi electrode and conventional potentiodynamic polarization methods. The results showed that the K₂Cr₂O₇ at 10⁻⁴ M after 30 min of exposure time behaves as the best inhibitor across the studied pH range. The efficiency of the Ce(dbp)₃ and CeCl₃ at 10⁻⁴ M was highly affected by the pH of the solution, where both cerium-based inhibitors gave similar protection to the K₂Cr₂O₇. Onen et al. [5] analyzed the use of titanium (iv) oxide (TiO₂) as an inhibitor for the corrosion of aluminum in H₂SO₄ solution. Various researchers have come to the same conclusion that some compounds that exist naturally can be successfully used as corrosion inhibitors. Avwiri

and Igbo [41] studied the effect of *Vernonia amygdalina* on the acidic corrosion of 3RS and 2S alloys using weight loss test. The results showed that the corrosion rate of the aluminum coupons in the HNO_3 and HCl solutions decreased with an increase in the exposure time due to passivation of the surface by Al_2O_3 and AlCl_3 respectively. The authors concluded that the studied inhibitor is an excellent inhibitor in HNO_3 and HCl solution at 0.2 and 0.4 g/l concentration at 29°C . Umoren et al. [42] studied the corrosion inhibition of aluminum in hydrochloric acid medium using exudate gum from *Raphia hookeri* as inhibitor at $30\text{--}60^\circ\text{C}$ by thermometric and weight loss methods. The experimental results showed that exudate gum is a good inhibitor of aluminum in hydrochloric acid medium and the efficiency of the inhibitor increases with an increase in concentration of the inhibitor but decreases with a rise in temperature. The authors concluded that *Raphia hookeri* performs as an inhibitor for aluminum corrosion in 0.1 M hydrochloric acid medium. Umoren and Solomon [38] investigated the influence of potassium iodide additives on the inhibition efficiency of *Aningeria robusta* extract for aluminum in 2 M hydrochloric medium using hydrogen evolution method at 30 and 60°C . Comparison between the corrosion rates data with and without additives was used to determine the inhibition efficiency by the authors. The result of the investigation showed that the *Aningeria robusta* extract is an inhibitor for acid corrosion of aluminum. *Lavandula angustifolia* was used as an inhibitor by [43]. The authors investigated the use of natural oil extracted from *Lavandula angustifolia* as an inhibitor for aluminum alloy in 3% sodium chloride medium using polarization measurements and weight loss techniques. The results showed that *L. angustifolia* oil acts as an effective inhibitor for the Al-3 Mg alloy corrosion in 3% NaCl medium at the temperature range studied. It was concluded that *Lavandula angustifolia* oil can be used to prevent pitting corrosion of aluminum. The combination of *Arachis hypogaea* natural oil was successfully used in the work of [37] as an inhibitor 2 M HNO_3 and 2 M HCl acids solutions. Bark extract have been successfully studied as corrosion inhibitor for aluminum in 1 M NaOH by [44]. Comparative study of different plant extract has been carried out by [45]. In order to contribute to the ongoing research, the current research work is focused on analyzing the effectiveness of novel corrosion inhibitors ferrous gluconate (FG) and zinc gluconate (ZG) for the corrosion of aluminum alloy in acidic ($0.5\text{ M H}_2\text{SO}_4$) and saline (3.5% NaCl) media.

5. Gluconate as corrosion inhibition for aluminum alloy

5.1. Behavior of aluminum alloy substrate in sodium chloride solution

The potentiodynamic polarization behavior of the received aluminum sample in saline solution is shown in **Figure 1**, where the polarization curve can be seen and the data obtained can be seen in **Table 1**.

In the sodium chloride solution, the aluminum sample gives a corrosion potential of -0.75893 V . The active corrosion path was formed as a result of the dissolution of the aluminum matrix. The surface of the tested aluminum coupon at different areas shows different dark shades, and this was examined by SEM/EDS. It is most likely that the darker areas are where the aluminum has not suffered severe corrosion from the sodium chloride, at those

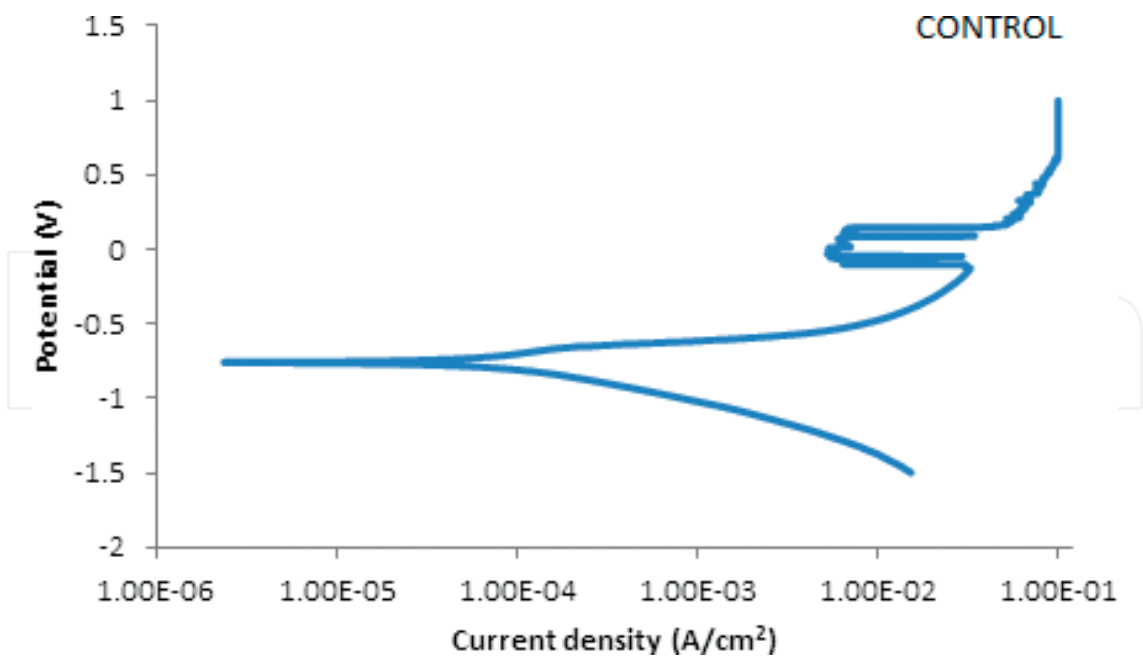
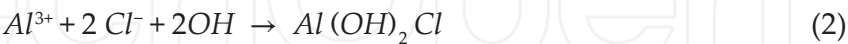
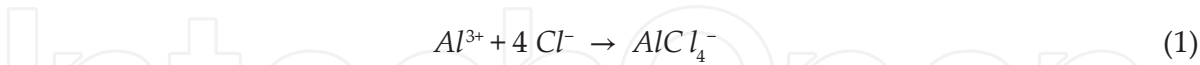


Figure 1. Linear polarization curve for aluminum alloy in sodium chloride solution [46].

areas surface oxides layers have been formed that impeded corrosion. At the whitish areas aluminum dissolution must have occurred the chloride ion has penetrated the matrix of the aluminum surface. This was confirmed by the EDS analysis on the different areas which revealed that the darker areas had a high Al peak while the whitish areas consist of O, Na, S, Fe and C. In the border between the whitish and the darker areas there was a band of hole which seems to be associated to the dissolution of the Al alloy as a result of the aggressiveness of the sodium chloride. This hole did not exist on the as received sample [46] (Figure 2).

The result show the adsorption of the oxide film, formation of basic hydrochloric aluminum salt which separates from the lattice and goes into the system:



The oxide film is thinned to the extent that aluminum ion can pass from the metal to the sodium chloride interface. The chloride ion gets entry by penetrating through the oxide film or diffusion of halide ion through the oxide film and attack the alloy.

S/N	C (% g/v)	I _{corr} (A/cm²)	β _c (V/dec)	β _a (V/dec)	LPR R _p (Ωcm²)	-E _{corr} (V)	CR (mm/yr)
1	0.0	8.59E-06	0.050867	0.080038	1572.3	0.75893	0.277870

Table 1. Polarization data for aluminum alloy in sodium chloride solution.

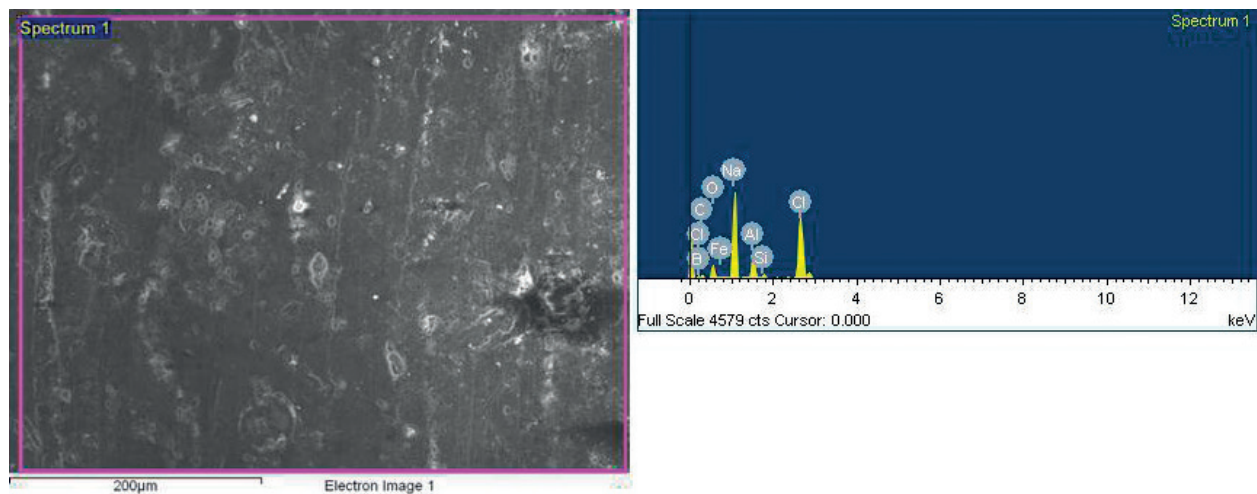


Figure 2. SEM/EDS spectra of corroded aluminum alloy in saline solution [46].

5.2. Behavior of aluminum alloy substrate in H_2SO_4 acid medium

The potentiodynamic polarization behavior of the as-received aluminum alloy sample in acid medium is shown in **Figure 3** where the polarization curve can be seen, the data obtained can be seen in **Table 2**.

The linear polarization curve determines the active or passive characterization of aluminum alloy in acid solution. In the acid solution, the aluminum sample gives a corrosion potential of -0.55960 V. The active corrosion path was formed as a result of the dissolution of the aluminum matrix.

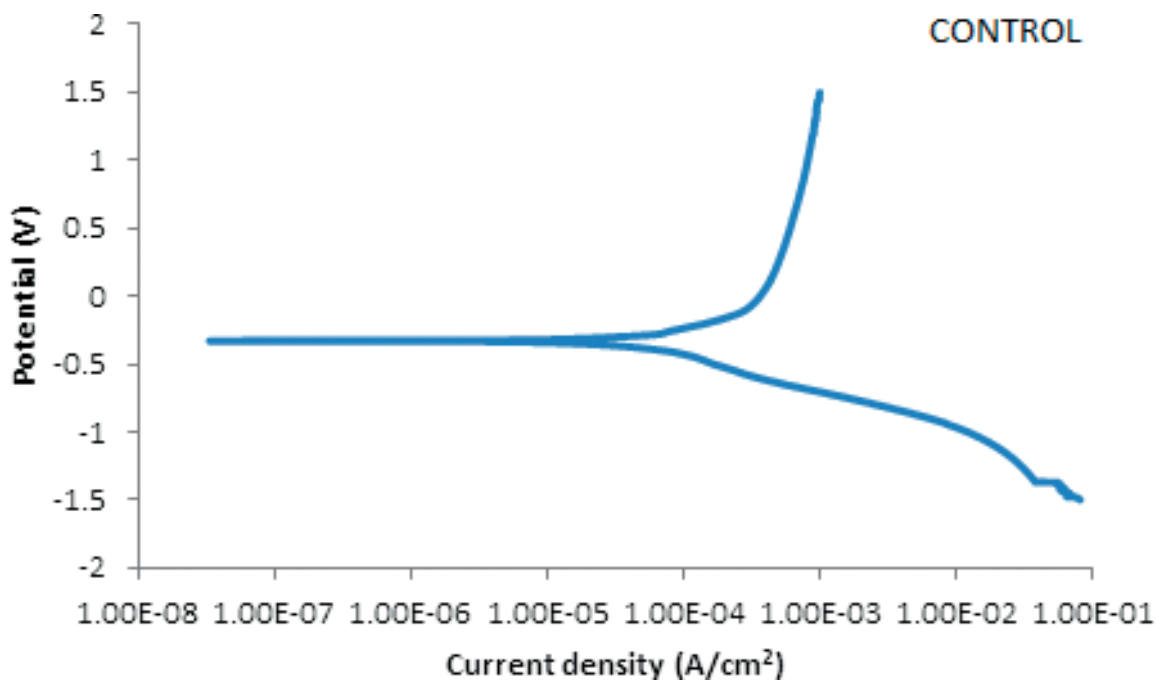


Figure 3. Tafel polarization curve for aluminum alloy in H_2SO_4 acid solution [46].

S/N	C (% g/v)	I _{corr} (A/cm ²)	β _c (V/dec)	β _a (V/dec)	LPR R _p (Ωcm ²)	–E _{corr} (V)	CR (mm/yr)
1	0.0	1.73E-05	0.025551	0.12493	532.51	0.33054	0.55960

Table 2. Polarization data for aluminum alloy in 0.5 M H₂SO₄ solution.

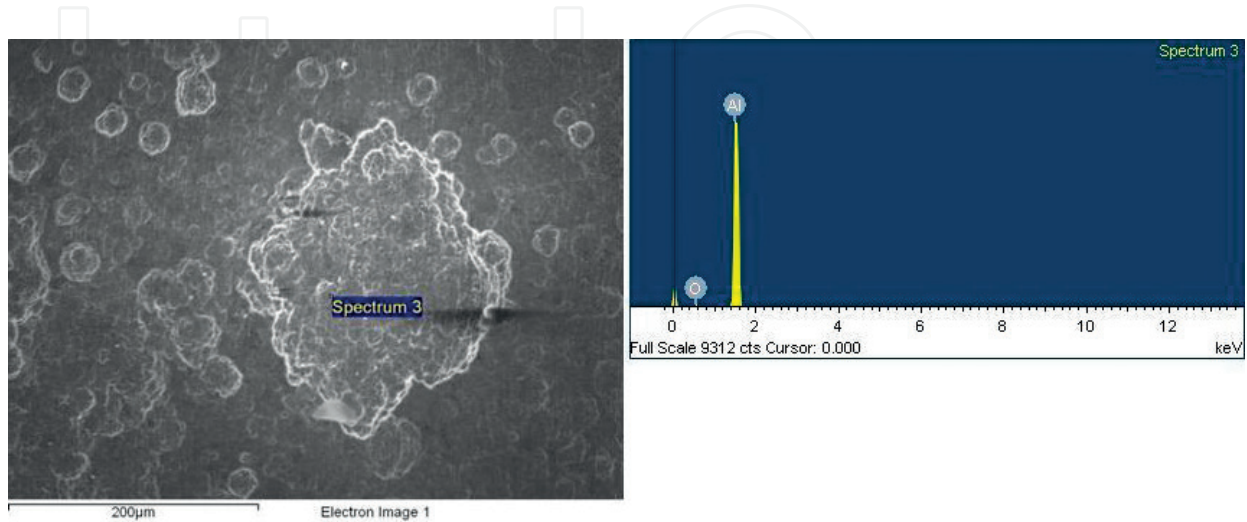
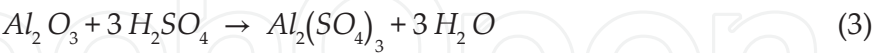


Figure 4. SEM/EDS spectra of corroded aluminum alloy in H₂SO₄ acid solution [46].

A morphological study of the surface of aluminum specimen in acid solution was carried out by SEM after immersion in the test solution for 28 days at 28°C [46]. **Figure 4** shows the SEM images of the aluminum surface after 28 days immersion in 0.5 M H₂SO₄ acid. A severely corroded surface was observed after immersion in the uninhibited system, due to corrosive attack of the acid solution. The corrosion product layer on the metal surface in uninhibited 0.5 M H₂SO₄ acid and the corrosion damage is clearly visible on the metal surface. The oxide film is thinned to the extent that aluminum ions can pass from the aluminum alloy to the solution interface.



The sulfuric ion gets entry by penetration through the oxide film and attack the metal.

6. Characterization of inhibited aluminum alloy in saline (3.5% NaCl) medium

The obtained results from weight loss and potentiodynamic polarization methods at different concentrations of ferrous gluconate (FG), zinc gluconate (ZG) and the synergistic effect of the two inhibitors in saline solution at 28°C are represented in Figures below.

6.1. Aluminum alloy in saline medium with ferrous gluconate (FG) as inhibitor

6.1.1. Weight loss method

Figure 5 is the plot of weight loss against exposure time for aluminum alloy coupons in saline environment in the absence and presence of different concentrations of FG at 28°C.

In the absence of FG, the weight loss increased with an increase in exposure time in 3.5% sodium chloride solution. The weight loss was 0.001 gm at the beginning of the analysis but increased with an increase in exposure time which gave a value of 0.011 gm after 28 days of exposure. In the presence of FG, the weight loss value was reduced given the highest value of 0.007 gm at the end of 28 days exposure time at all the concentrations of inhibitor studied. This clearly indicates a 36% reduction in weight loss value in the presence of FG when compared to the value in the absence of FG [47, 49].

Figure 6 shows the graph of corrosion rate of aluminum alloy coupons in the absence and presence of varied concentrations of FG in 3.5% NaCl solution at 28°C.

Observation made indicates that corrosion rate of aluminum alloy reduced in the presence of all the different concentrations of FG considered. In the presence of 0.5% g/v concentration of FG, the corrosion rate value was 0.051 mm/yr at the end of 28 days exposure time compared with the absence of FG which gave 0.110 mm/yr at the end of 28 days of exposure [47, 49]. This shows 54% reduction in corrosion rate value compared with the absence of FG. It can be deduced that FG inhibits the corrosion of aluminum alloy in saline solution. Also shown in **Figure 7** is the graph of percentage inhibition efficiency (%IE) with exposure time in the presence of different concentrations of FG.

A reduction in IE of FG from 100% depending on the concentration of FG added to the corrosive environment was observed. The inhibition efficiency at 0.5% g/v concentration

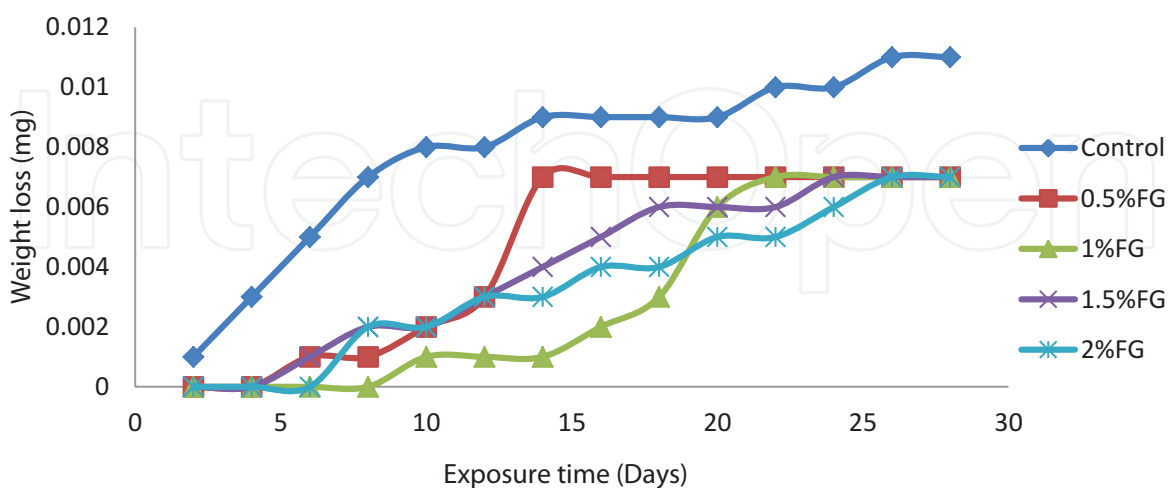


Figure 5. Weight loss versus exposure time for aluminum alloy immersed in 3.5% NaCl solution with varied ferrous gluconate addition [47].

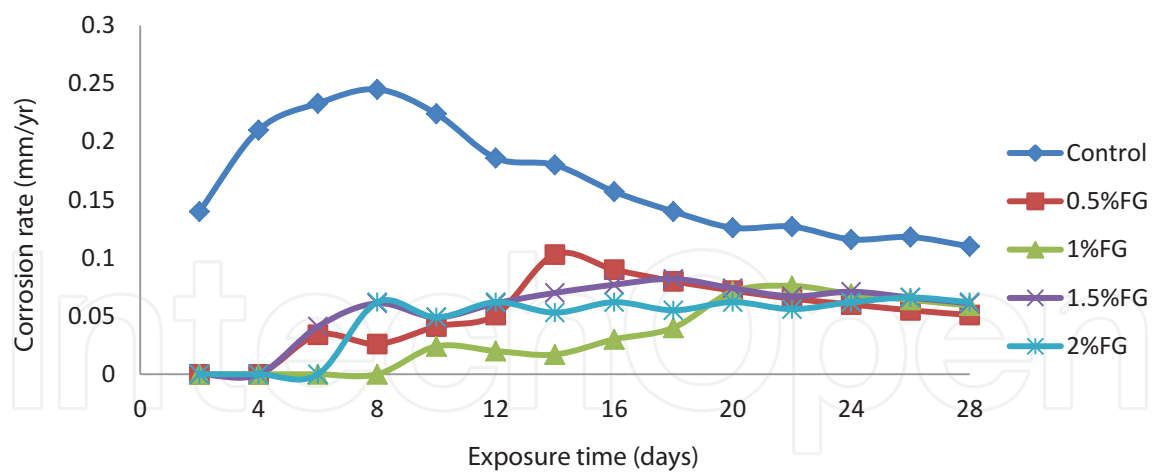


Figure 6. Corrosion rate versus exposure time for aluminum alloy immersed in 3.5% NaCl solution with varied ferrous gluconate addition [47].

of FG reduced to 54%, 1.0% g/v reduced to 46%, 1.5% g/v reduced to 45% and 2.0% g/v reduced to 44% at the end of 28 days exposure time to the corrosive environment. The optimum inhibition efficiency was observed at 1.0% g/v concentration of FG in 3.5% NaCl solution at 28°C.

6.1.2. Adsorption studies

The Langmuir adsorption isotherm was found to best describe the adsorption behavior of FG as inhibitor. Plot C/θ against C yield straight lines with regression coefficient, R^2 equals 1. The results plotted in **Figure 8** suggest that FG in 3.5% NaCl solution at 28°C obeyed Langmuir adsorption isotherm.

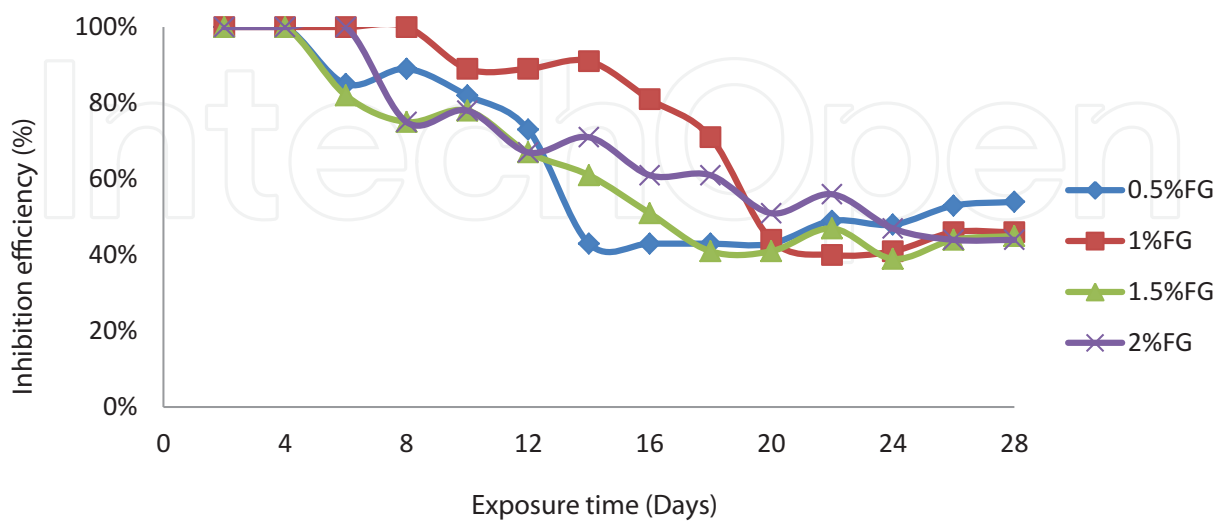


Figure 7. Inhibition efficiency versus exposure time for aluminum alloy immersed in 3.5% NaCl solution with varied ferrous gluconate addition [47].

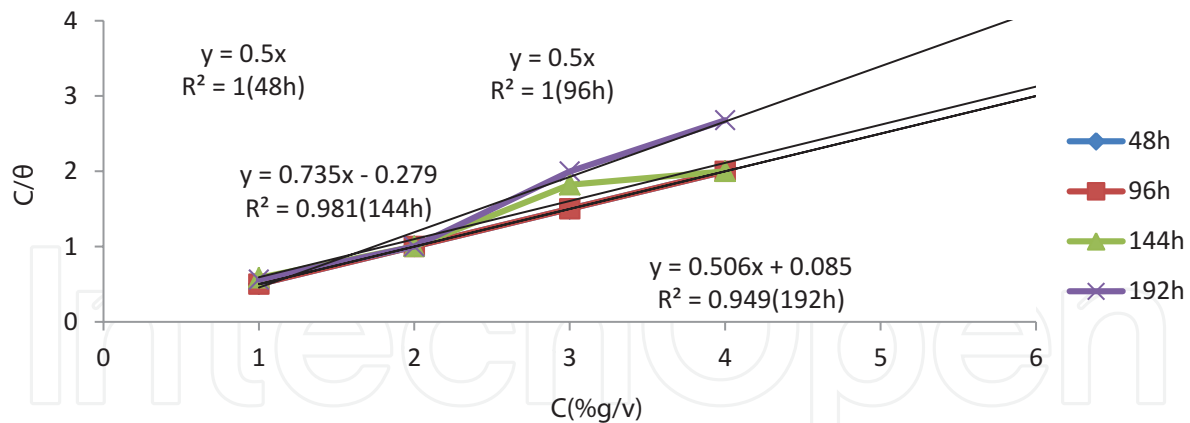


Figure 8. Langmuir isotherm for the adsorption of different concentrations of FG on aluminum alloy surface in 3.5% NaCl solution obtained at 28°C [47].

6.1.3. Microstructural characterization of FG inhibited aluminum alloy in saline medium

The morphology of the test sample showing the inhibitive action of ferrous gluconate in saline solution with 1.0% g/v concentration of FG after weight loss experiment is shown in **Figure 9**. The severity of the damage is much less when compared with the morphology of the sample in the absence of FG. The effective corrosion inhibition of FG could be attributed to the film formed on the aluminum alloy surface which acts as a barrier between the aluminum alloy and the corrosive environment boundary, thereby preventing further corrosion reaction. From the EDS in **Figure 9**, the presence of oxygen and other elements is as a result of ferrous gluconate constituent [47].

In the presence of 2.0% g/v concentration of FG, the corrosion is slightly reduced with little corrosion product on the aluminum alloy surface when compared with the morphology of the aluminum alloy in the absence of FG. This clearly revealed that FG is a corrosion inhibitor for the aluminum alloy in acidic solution. The effective corrosion inhibition of FG could

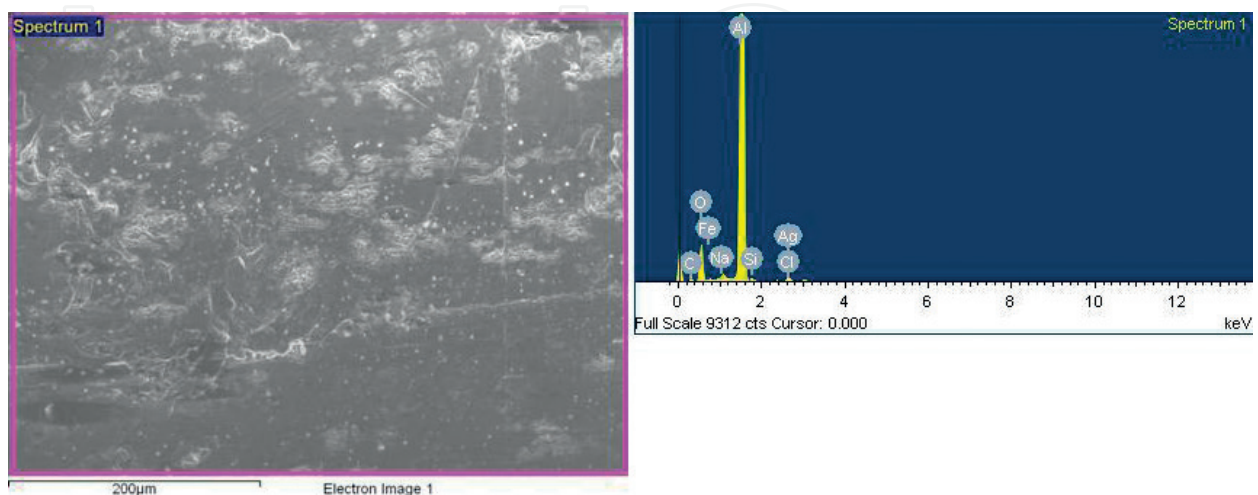


Figure 9. SEM/EDS spectra of corroded aluminum alloy in the presence of FG [47].

be attributed to the film formed on the surface of the sample. The EDS in **Figure 9** clearly shows the presence of carbon, oxygen indicating the formation of oxide films as confirmed by Raman spectroscopy. Other elements are also present which is as a result of ferrous gluconate constituent.

6.1.4. Potentiodynamic polarization method

Table 3 shows the electrochemical corrosion parameters that is, potentiodynamic polarization-corrosion potential (E_{corr}), linear polarization resistance (R_p), anodic and cathodic Tafel slopes (β_a , β_c), corrosion rate (CR) and potentiodynamic polarization corrosion-current density (i_{corr}) obtained by extrapolation of the Tafel lines.

Figure 10 gives the potentiodynamic polarization curves for the inhibition of aluminum alloy in the absence and presence of different concentrations of ZG in 0.5 molar sulfuric acid solutions at 28°C. From **Table 3**, it can be concluded that the corrosion current density (i_{corr}) values reduced in the presence of all the concentrations of ZG studied. The anodic and cathodic values were observed to change in the presence of all the different concentrations of ZG studied in 0.5 M H_2SO_4 solution. The polarization resistance (R_p) values increased and corrosion rate (CR) values decreased in the presence of inhibitor. Also, no definite trend was observed in the corrosion potential (E_{corr}) values in the presence of inhibitor [47]. This result showed the influence of ZG on aluminum alloy in 0.5 M H_2SO_4 solution and the ZG acts as a mixed type inhibitor.

6.2. Synergetic effect of the two inhibitors (FG+ZG) on aluminum alloy in H_2SO_4 acid medium

6.2.1. Weight loss method

Figure 11 shows the variation of weight loss with exposure time for aluminum alloy coupons in 0.5 molar sulfuric acid solution in the absence and presence of different concentrations of FG and ZG in the same proportion at 28°C. The Figure shows an increase in weight loss value in the absence of inhibitors with an increase in exposure time. In the presence of inhibitors, there was a decrease in weight loss of the aluminum alloy coupons with the following values after 28 days exposure time to the corrosive medium; 0.027 gm, 0.025 gm, 0.022 gm and 0.020 gm

S/N	C (% g/v)	I_{corr} (A/cm ²)	β_c (V/dec)	β_a (V/dec)	LPR R_p (Ωcm^2)	$-E_{\text{corr}}$ (V)	CR (mm/yr)
1	0.0	1.73E-05	0.025551	0.124930	5.33E+02	0.33054	0.559600
2	0.5	6.46E-06	0.054932	0.032904	1.38E+03	0.33054	0.209090
3	1.0	5.43E-06	0.042048	0.035871	1.55E+03	0.33054	0.175710
4	1.5	6.30E-09	0.892180	1.727600	4.06E+07	0.34318	0.000206
5	2.0	3.78E-06	0.172780	0.072640	5.87E+03	0.35751	0.123690

Table 3. Polarization data for ZG inhibited aluminum alloy in 0.5 M H_2SO_4 solution.

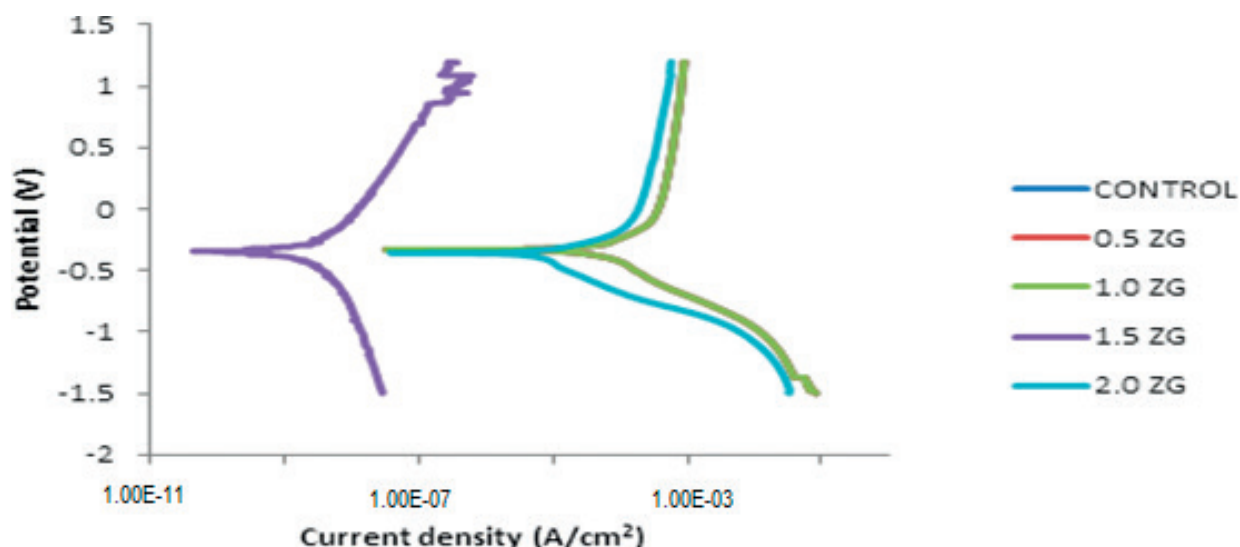


Figure 10. Tafel polarization curves for aluminum alloy in 0.5 M H_2SO_4 solution in the absence and presence of different concentrations of ZG at 28°C [48].

at 0.5:0.5, 1.0:1.0, 1.5:1.5 and 2.0:2.0 g/v concentrations of inhibitors respectively. These values translated to 27% for 0.5:0.5 g/v, 32% for 1.0:1.0 g/v, 41% for 1.5:1.5 g/v and 46% for 2.0:2.0 g/v when the weight loss values in the presence of inhibitors were compared with the values in the absence of inhibitors. The Figure also denotes that increase in concentration of the inhibitor leads to a decrease in the weight loss of the aluminum alloy coupon.

The variation of corrosion rates of aluminum alloy coupons exposed to 0.5 M H_2SO_4 solution at 28°C in the absence and presence of different concentrations of FG and ZG are presented in **Figure 11**. The Figure shows that in the absence of inhibitors, the corrosion rate of aluminum alloy decreased from 0.395 to 0.346 mm/yr after 28 days exposure time to the corrosive environment (**Figure 12**).

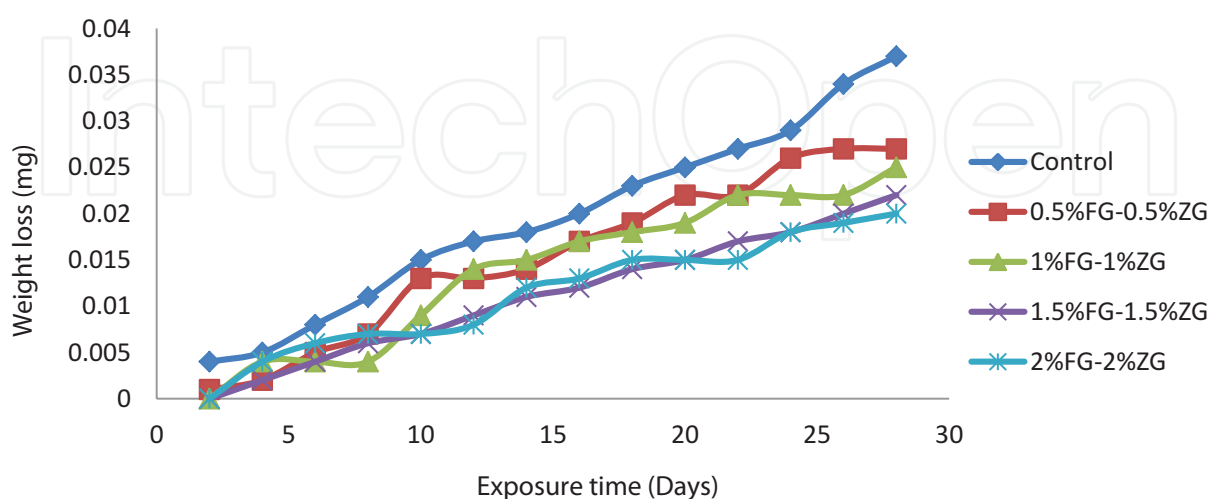


Figure 11. Weight loss versus exposure time for aluminum alloy immersed in 0.5 M H_2SO_4 solution with varied ferrous gluconate and zinc gluconate additions [46].

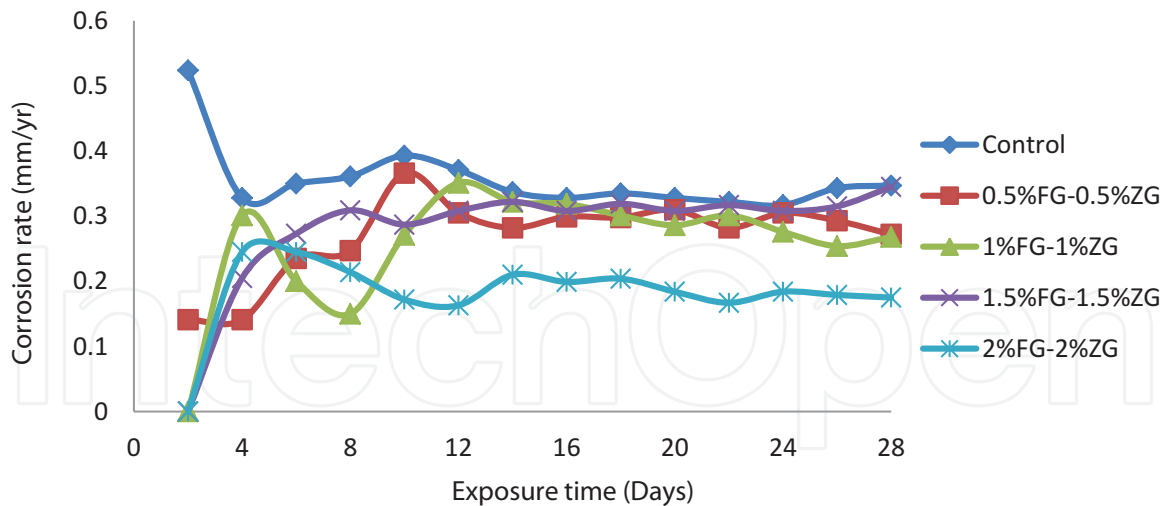


Figure 12. Corrosion rate versus exposure time for aluminum alloy immersed in 0.5 M H_2SO_4 solution with varied ferrous gluconate and zinc gluconate additions [46, 50–51].

The graph shows a sinusoidal trend. In the presence of inhibitors, the corrosion rate values was reduced from 0.346 to 0.272 mm/yr at 0.5:0.5 g/v concentration of FG-ZG, 0.268 mm/yr at 1.0:1.0 g/v, 0.345 mm/yr at 1.5:1.5 g/v and 0.175 mm/yr at 2.0:2.0 g/v. The percentage reduction in the corrosion rate value of aluminum alloy after 28 days of exposure in the presence of different concentrations of inhibitors are 21% for 0.5:0.5 g/v, 23% for 1.0:1.0 g/v, 0.3% for 1.5:1.5 g/v and 49% at 2.0:2.0 g/v.

Figure 13 shows the variation of percentage inhibition efficiency (%IE) against exposure time with different concentrations of inhibitors at 28°C. From the results, it was observed that the inhibition efficiency increased with an increase in the concentration of the inhibitors. The optimum inhibition efficiency was observed at 0.5 g/v concentration of the inhibitors.

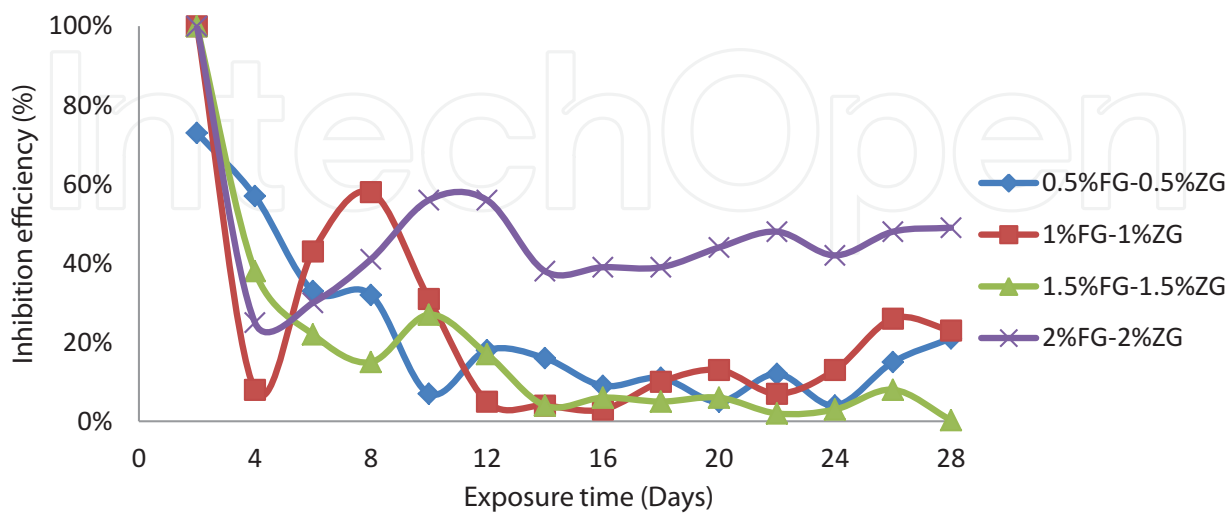


Figure 13. Inhibition efficiency versus exposure time for aluminum alloy immersed in 0.5 M H_2SO_4 solution with varied ferrous gluconate and zinc gluconate additions [46].

6.2.2. Adsorption studies

The Langmuir adsorption isotherm provides the best description for the adsorption behavior of the synergistic effect of FG and ZG as inhibitors. Plot C/θ against C yield a straight line with regression coefficient, R^2 close to 1. The result plotted in **Figure 14** suggests that the inhibitors in 0.5 M H_2SO_4 solution at 28°C obeyed Langmuir adsorption isotherm.

6.2.3. Potentiodynamic polarization method

Table 4 shows the electrochemical corrosion kinetics parameters: polarization resistance (R_p), potentiodynamic polarization-corrosion potential (E_{corr}), potentiodynamic polarization corrosion-current density (i_{corr}), corrosion rate (CR), anodic and cathodic Tafel slopes (β_a and β_c) obtained by extrapolation of the Tafel lines. **Figure 15** shows the cathodic and anodic polarization curves obtained for aluminum alloy in 0.5 molar sulfuric acid solution in the absence and presence of different concentrations of FG and ZG at 28°C.

The results showed a decrease in corrosion current density (i_{corr}) and corrosion rate (CR) values in the presence of different concentrations of inhibitors studied. The corrosion potential (E_{corr}) and polarization resistance (R_p) values increased in the presence of inhibitors. Shifts in anodic and cathodic region suggest the inhibitor is a mixed type corrosion inhibitors for aluminum alloy in 0.5 M H_2SO_4 solution at 28°C.

6.3. Correlation between experimental results and analyses (aluminum)

6.3.1. Weight loss and electrochemical corrosion test methods (aluminum)

The percentage inhibition efficiency (%IE) of aluminum alloy in 3.5% sodium chloride solution and 0.5 molar sulfuric acid environments in the presence of different concentrations of FG, ZG and the synergistic effect of the two inhibitors was obtained from weight loss and potentiodynamic

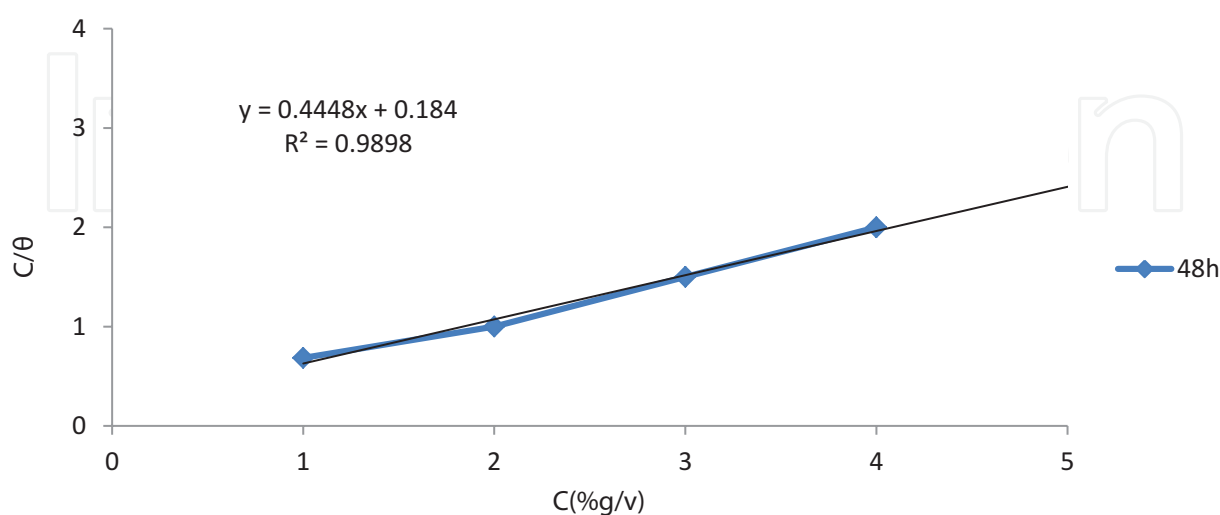


Figure 14. Langmuir isotherm for the adsorption of different concentrations of FG and ZG on aluminum alloy surface in 0.5 M H_2SO_4 solution obtained at 28°C [46].

S/N	C (% g/v)	I _{corr} (A/cm ²)	β _c (V/dec)	β _a (V/dec)	LPR R _p (Ωcm ²)	-E _{corr} (V)	CR (mm/yr)
1	0.0	1.73E-05	0.025551	0.124930	5.33E+02	0.33054	0.559600
2	0.5	4.29E-06	0.033853	0.025551	1.47E+03	0.33054	0.138900
3	1.0	2.71E-06	0.020610	0.059142	2.45E+03	0.11486	0.087732
4	1.5	6.30E-09	0.892180	1.727600	4.06E+07	0.34318	0.000206
5	2.0	2.57E-07	0.043434	0.263020	6.30E+04	0.99295	0.008324

Table 4. Polarization data for FG and ZG inhibited aluminum alloy in 0.5 M H₂SO₄ solution.

polarization methods. The data computed for the %IE using linear polarization resistance (LPR), potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic polarization-corrosion current density (PP-icorr) and weight loss method (WLM) are presented in the Figures above at different concentrations of inhibitors studied. From the given graphs, it is evident that obtained data from the different methods are in good correlation at all the concentrations of inhibitors studied.

6.3.2. Surfaces analyses (aluminum alloy)

From the SEM/EDS micrographs, aluminum alloy in acidic medium was observed to be more corrosive than aluminum alloy in sodium chloride medium after the immersion tests in both environments in the absence of inhibitors. Significant difference in the morphology of the as-received and the corroded samples of aluminum alloy in the absence and presence of inhibitors revealed that the inhibitors was able to hinder the dissolution of aluminum alloy in all the environments investigated. More uniform films were observed on the surfaces of

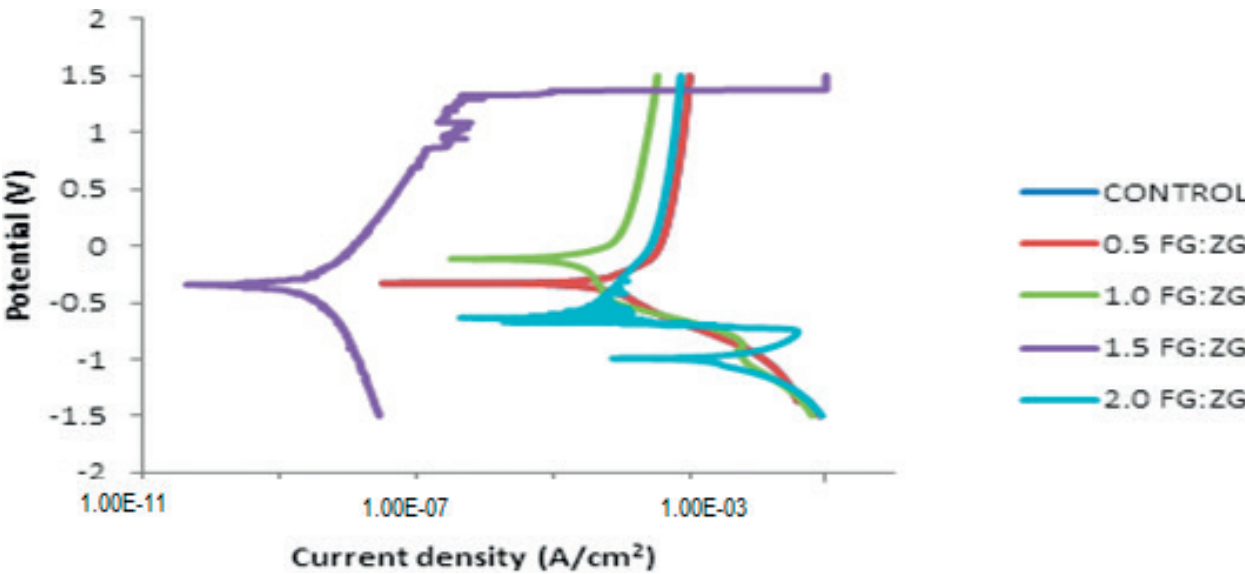


Figure 15. Tafel polarization curves for aluminum alloy in 0.5 M H₂SO₄ medium in the absence and presence of different concentrations of FG and ZG at 28°C [46].

the aluminum alloy in sulfuric acid solution compared to sodium chloride solution, which implied that the corrosion rate in acidic medium is higher when compared to corrosion rate in sodium chloride medium in the presence and absence of inhibitors.

7. Conclusions

The following conclusions have been drawn from this research;

- The aluminum alloy exhibited similar corrosion behavior in the presence of different concentrations of inhibitors in the solution studied, with different corrosion resistances in the different solutions which was confirmed from the similar trend from corrosion rates and inhibition efficiency of the materials from weight loss and potentiodynamic polarization curves.
- In saline environment in the presence of different concentration of inhibitors, the corrosion resistant of aluminum alloy was significantly different, which was evident by their corrosion rates and inhibition efficiency values. FG performed best at 1.0% g/v concentration in 3.5% NaCl solution which gave inhibition efficiency value of 100% from the beginning of the analysis to the 8th day of exposure time to the corrosive medium. ZG performed best at 2.0% g/v concentration which gives inhibition efficiency value of 100% from the beginning of the analysis to the 14th day of exposure time to the corrosive solution and the inhibition efficiency of the synergism of the two inhibitors was 100% from the beginning of the analysis to the 10th day of exposure time to the corrosive medium.
- It could be concluded that ZG performed best in 3.5% NaCl solution. The inhibitors performed fairly well in 0.5 M H_2SO_4 solution. The corrosion rates and inhibition efficiency values obtained from the weight loss and potentiodynamic polarization methods show good agreement.
- The main task of this research work has been accomplished. The optimum concentrations for the application of the inhibitors which should be useful guide for corrosion engineers have been obtained.
- It can be seen from above that FG, ZG and FG+ZG acts as a good corrosion inhibitor for aluminum alloy in saline and acid environments with the following final deduction: Aluminum alloy: in both test environments, the inhibitive performances of the inhibitors are excellent. Finally, the inhibitors have been established to be practically reliable and effective as demonstrated by the performance characteristics of the inhibitors that were used in this study.

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