CORROSION INHIBITION OF SOME ALLOYS IN ACIDIC MEDIA USING INORGANIC (K2CrO4) AND ORGANIC (C6H5.NH2) INHIBITORS

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ABSTRACT

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| Corrosion of metal is an electrochemical process that promotes the deterioration of metals. This phenomenon can be controlled or mitigated through the use of chemical inhibitors. Research in the use of chemical inhibitors is gaining wider interest. This study describes the use of inorganic (potassium chromate, K2CrO4) and organic (aniline, C6H5.NH2) inhibitors, as corrosion control for cold steel and aluminium alloys in acidic media using varying inhibitor concentrations. Experiments using weight loss (WL) techniques were adopted to evaluatethe extent of corrosion of the metals. The WL data were recorded for 1-7 days immersion period, and their efficiencies calculated in percentages, I.EM (%). For an optimum inhibition, the inhibitors were added above a certain minimum concentration. Corrosion rate (CR) was found to be higher (0.07) in 11g/L than in 2g/L concentration (0.02) in K2CrO4 for the aluminium metal. Similarly, in the presence of the potassium chromate inhibitor, the corrosion rate in cold steel varied slightly (0.04; 0.06) in the 11g/L and 2g/L concentrations respectively. The I.EM (%) was found to increase from the 2.0g/L to 11.0g/L immersed in HCl and HNO3at 0.5 M respectively. Corrosion inhibitions were found to increase with increase in concentrations of inhibitors. The results obtained indicated better inhibitor efficiency in the higher concentration than in the lower concentration in the presence of the inorganic and organic inhibitors in cold steel and aluminium metals respectively. The highest I.EM (%), (92.41 %) was recorded for potassium chromate at 11g/L, whereas, the least I.EM (%) was recorded for potassium chromate (37.90 %) at 2g/L. The results showed that the application of higher concentrations of both inorganic and organic inhibitors in the metal-inhibitor-media interaction yielded greater protection and significantly mitigated the corrosion reactions for cold steel and Aluminium in both acidic media. These results may find wider applicability in the formulation of appropriate anti-corrosion system by scientists, policy-makers and environmental stakeholders on critical assets especially in the petroleum and allied chemical industries. . |

*Keywords: Corrosion, Inhibitors, Potassium Chromate, Aniline, Percent Efficiency*

1. INTRODUCTION

Corrosion is the deterioration of the intrinsic properties in a metal due to chemical reactions with the environment (Harsimran *et al.,* 2024; Popoola *et al*., 2013). The increasing cost associated with corrosion impacts on critical assets and the resultant losses are quite alarming and require regular checks (Al Jahdaly *et al.,*2022). Although cold steel is usually attacked by corrosion, it is one of the most commonly utilized metal materials due to its physical strength, mechanical properties and durability (Dong *et al.,* 2021). Besides, as a result of its simple processing and cost-effective production, steels are widely and extensively used in various industries (Shwetha *et al.,* 2024). Furthermore, a combination of thermal oxidation and chemical modification has been applied in creating a superhydrophobic surface on metal alloys including Aluminium (Nyong *et al.*, 2023; Nyong *et al*., 2017). The surfaces of aluminum and its alloys are often exposed to reactive liquids and oils in various situations, which can induce surface tarnishing, corrosion and fouling thereby reducing their time-span of usefulness (Nyong *et al.,* 2019).

The direct and indirect impacts of corrosion to industrial facilities and society can be enormous (Awaka-ama, 2012; Al-Amiery, 2024). For instance, structural damage due to metal fatigue and failure of metallic assets in the petroleum industry can result in contamination of the environment, posing a potential risk to the ecosystem and human health (Awaka-ama *et al.,* 2024a). Hence, the use of appropriate strategies for tackling corrosion phenomenon is necessary to ensure sustainable development. Proper corrosion management also mitigates other safety hazards, linked indirectly with health, quality of environment and carbon footprints resulting in increased public and industrial safety, reliable performance, structural integrity, maximized assets life, long term viability and cost-effective operations.

Thus, corrosion is a costly legacy challenge in industries, with far-reaching consequences. In industrial settings such as the various oilfield operations, where corrodible surfaces abound, contact of fluids with metal is inevitable: Acid cleaning, acid stimulation, drilling muds, oil storage tanks, steam generators, technological vessels, natural gas plants, refineries, product pipelines and equipment, pickling, descaling operations, acid solutions are widely used on metal substrates to achieve the intended purposes (Ajayi *et al*., 2011; Omotosho *et al*., 2011). These processes require adequate checks to avoid acid damage on metallic materials.

In these sectors, availability of corrosion agents such as water, oxygen, humidity, acids, oils, some solids particles, base salts, fluid chemicals, ammonia and gaseous materials, sulphur and hydrogen sulphide can initiate corrosion when in direct contact, chemical leakage, oil pipelines breakdown etc. Even the presence of some trace metals in crude oil acting as catalyst poison can be corrosive thus easily blocking the process equipment (Awaka-ama *et al.,* 2024b; Fayomi *et al.,* 2019).This is because metals are thermodynamically stable in their natural state (compounds or ores) but when additional processes are provided to convert them to useable metals they become thermodynamically unstable and tend to revert to their natural states to regain stability through corrosion process (Harsimran *et al.,*, 2021). Corrosion agents such as stress and high temperatures are favorable conditions for this reverse process.To this end, the effect of temperature on the morphology and growth kinetic of the oxides formed through the thermal oxidation of some metal alloys has been reported (Nyong *et al.,* 2022).

Generally, metal corrosions are electrochemical in nature, involving exchange of electrons from anode to cathode in a given conductive solution (Perez, 2024). With this basic knowledge, emerging innovations and technological advances have been developed to address corrosion phenomenon (Shwetha *et al.,* 2024).These approaches often include improved structural designs (Navarro *et al,* 2019), cathodic protection (Chen *et al.,* 2009; Yabuki *et al*., 2018), protective coatings (Ubuo *et al.,* 2023), electroplating (Shakiba, *et al.,*2022, galvanizing (Lozrt, J., Votava*et al.,* 2021), and the use of corrosion inhibitors (Kadhim*et al.,*2021). Among these traditional methods, the use of inhibitors has been reported to be the most affordable method in inhibiting corrosion (Shwetha*et al.,* 2024).

According to National Association of Corrosion Engineers (NACE) International, corrosion inhibitor is a chemical compound that, when added in certain concentrations to an environment, effectively decreases the corrosion rate or stops the corrosion. (Zehra *et al.,* 2022). In broader perspective, its applications in various segments of the industry, including oil wells, emphasizes the importance and impact of corrosion in these sectors. Film-forming inhibitors are known to demonstrate unrivalled performance as a method of defense for mild steel in an acidic environment (Zeino *et al*., 2018; Umoren and Eduok, 2016). The film-forming inhibitors are used in industries to create a molecular layer right on the surface of the steel and aliphatic tail as a second layer in hydrocarbon to prevent the water from contacting the steel surface and causing corrosion (Yadav *et al.*, 2010). Organic compounds function through the adsorption on the surface of the metal to prevent the occurrence of corrosion (Tamalmani and Husin, 2020; Chen *et al*., 2023)

This study describes the development of a measurable and testable data towards the control of corrosion induced damage of metallic materials, through the use of inhibitor systems focusing on investigation of the interfacial conditions of the metals in the presence of inorganic and organic inhibitors, through evaluation of the metal-inhibitor-media interaction mechanism. Simulations using weight loss (WL) techniques were adopted to evaluate different inhibitors efficiency.

2. material and methodS

**2.1 Materials Preparation**

The materials used for the study were cold rolled steel and aluminium alloy sheets. Cold rolled steel was used because of its versatility as common material for construction. Aluminium and its alloys are utilized mainly in light weight applications and they offer some corrosion resistance due to their affinity for oxygen to form a passive oxide layer. The sheets were mechanically pressed cut to form different coupons each of dimension, 4 x 3cm. They were subjected to chemical treatment and each steel coupon was degreased by washing with ethanol, dried with acetone and preserved in a desiccator. The various reagents used in the experiments were manufactured by Sigma Aldrich, UK and included HCl as well as inhibitors, Potassium Dichromate (K2CrO4) and Phenylamine (C6H5NH2); which were all analar grade purity. Deionized water was used in the preparation of all solutions of inorganic and organic inhibitor concentrations using appropriate standard method.

**2.2 Media or corrodents Environment**

The media or corrodents utilized in this study were HCl at 0.5 M concentrations respectively and were used to evaluate the inhibitor efficiency (I.EM%). The volumes of the test solutions were set at 100 ml. The vessel used for the reactions were a bottom-flasks and the procedure for determination of corrosion behavior using this method has been described by other authors as reported by Ebenso (2003) and Umoren *et al.* (2006, 2007).

**2.3 Weight Loss (WL)**

The effectiveness of the inorganic and organic inhibitors to inhibit corrosion can be evaluated by implementing weight loss method. This corrosion rate monitoring approach finds merit due to its simplicity and reliability (Shweta *et al*, 2024). The metal samples were weighed both before and after they were immersed in acidic solution in the presence of 2g/L and 11 g/L of K2CrO4and C2H5.NH2as inhibitors. This enabled the computation of the weight loss of the pre-cleaned and dried cold rolled steel and aluminium samples. The weight loss was determined by retrieving the metal coupons at 24 h interval progressively for 168 h (7 days). The mean results were obtained and used to calculate the samples corrosion rate (CR).

**2.4 Determination of Corrosion Rate (CR)**

After obtaining the weight loss data, it was possible to determine the corrosion rate (CR) as stated below (ASTM G 1-03):

$$Corrosion Rate \left(CR\right)=87.6\*\frac{W}{tAD}$$

Where:

A = Area of sample in square cm (cm2)

T = Time of immersion (Exposure period) in hours

D = Density of samples in g/cm-3

W = Sample’s corrosion weight loss in grams

Using this relationship, the corrosion rate (CR) was determined with units in cm/hour (cm/hr).

**2.5 Determination of Inhibition Efficiency I.EM (%)**

Determination of Inhibitor Efficiency (I.EM %) was obtained from equation below as described by (*Ebenso et al.*, 2004; Omotosho *et al.,* 2012a)

$$Mass based Inhibitor Efficiency \left(I.EM\%\right)=\frac{CR\_{cont}-CR\_{inh}}{CR\_{cont}}\*100$$

Where:

CRcont = Corrosion rate of metal sample in acid media (in the absence of inhibitor)

CRinh = Corrosion rate of metal sample in the presence of the inhibitor and the acid

3. results and discussion

**3.1 Results**

The results obtained from our series of experiments are presented in the Tables 1, 2 and 3 below. In these Tables 1, 2 and 3 the weight losses obtained, the corrosion rates calculated and the inhibition efficiencies obtained when cold rolled steel and aluminum samples are exposed to the various acidic media in the presence of various concentrations of Potassium Chromate and Aniline solutions, serving as inhibitors, are highlighted respectively.

**Table 1. Weight loss (g), Corrosion Rate, Percent Inhibition Efficiency (% I.E) for the corrosion of cold Steel in different concentrations of Potassium chromate solutions for HCl acidic medium for various time durations**

|  |  |
| --- | --- |
| **Time** | **Potassium chromate solution** |
| 2.0g/L | 11.0 g/l |
| Weight Loss (g) | Corrosion Rate | Percent Inhibition Efficiency (% I.E) | Weight Loss | Corrosion Rate | Percent Inhibition Efficiency (% I.E) |
| 24 | 1.72 | 0.066 | 37.90 | 1.29 | 0.049 | 53.77 |
| 48 | 1.50 | 0.029 | 77.00 | 1.25 | 0.024 | 75.47 |
| 72 | 1.27 | 0.016 | 84.90 | 1.19 | 0.015 | 85.96 |

**Table 2. Weight loss (g), Corrosion Rate, Percent Inhibition Efficiency (% I.E) for the corrosion of Cold Steel in different concentrations of Aniline solutions for HCl acidic medium for various time durations**

|  |  |
| --- | --- |
| **Time** | **Aniline solution** |
| 2.0g/L | 11.0 g/l |
| Weight Loss (g) | Corrosion Rate | Percent Inhibition Efficiency (% I.E) | Weight Loss | Corrosion Rate | Percent Inhibition Efficiency (% I.E) |
| 24 | 1.44 | 0.056 | 48.01 | 0.23 | 0.0089 | 91.60 |
| 48 | 1.35 | 0.026 | 75.47 | 0.19 | 0.0074 | 93.02 |
| 72 | 1.31 | 0.017 | 85.96 | 0.16 | 0.0062 | 94.15 |

**Table 3. Weight loss (g), Corrosion Rate, Percent Inhibition Efficiency (% I.E) for the corrosion of Aluminum in different concentrations of Potassium chromate solutions for HCl acidic medium for various time durations**

|  |  |
| --- | --- |
| **Time** | **Potassium chromate solution** |
| 2.0g/L | 11.0 g/l |
| Weight Loss (g) | Corrosion Rate | Percent Inhibition Efficiency (% I.E) | Weight Loss | Corrosion Rate | Percent Inhibition Efficiency (% I.E) |
| 24 | 0.42 | 0.047 | 59.55 | 0.21 | 0.024 | 77.14 |
| 48 | 0.51 | 0.029 | 72.38 | 0.32 | 0.018 | 82.86 |
| 72 | 0.63 | 0.024 | 77.14 | 0.43 | 0.016 | 84.76 |

**Table 4. Weight loss (g), Corrosion Rate, Percent Inhibition Efficiency (% I.E) for the corrosion of Aluminum in different concentrations of Aniline solutions for HCl acidic medium for various time durations**

|  |  |
| --- | --- |
| **Time** | **Aniline** |
| 2.0g/L | 11.0 g/l |
| Weight Loss (g) | Corrosion Rate | Percent Inhibition Efficiency (% I.E) | Weight Loss(g) | Corrosion Rate | Percent Inhibition Efficiency (% I.E) |
| 24 | 0.40 | 0.045 | 57.55 | 0.28 | 0.032 | 69.52 |
| 48 | 0.48 | 0.027 | 74.53 | 0.18 | 0.016 | 84.76 |
| 72 | 0.59 | 0.022 | 79.25 | 0.11 | 0.0041 | 96.13 |

**3.2 Discussion**

Corrosion of the metallic alloys were evaluated in HCl and HNO3 acidic media using varying inhibitor concentrations of potassium chromate (K2CrO4) (inorganic), and aniline (C6H5.NH2) (organic). Weight loss (WL) data for the metallic materials (cold steel and aluminium) were used to evaluate the inhibitor effect on corrosion of the metals.

**3.2.1 Weight Loss (WL)**

The cooled rolled iron and aluminum used in this corrosion tests all experienced weight loss in the HCl medium. This loss of weight is simply as a result of the oxidation of the metals in the presence of the HCl. At the initial conditions, without the addition of any inhibitor, we express the oxidation processes in both materials by means of the chemical equations expressed below:

$Fe \left(in cold steel\right)+2HCl\rightarrow FeCl\_{2}+H\_{2}$ (1)

$Al+3HCl \rightarrow AlCl\_{3}+ 1.5H\_{2} $(2)

On a comparative basis, the weight losses in both metals reduced with increase in the concentrations of the inhibitive chemical additives. In this case, the weight losses observed when the concentrations of the inhibitive chemical additives were increased from 2.0g/l to 11 g/l showed that the least weight losses were observed at the 11 g/l concentration value for Potassium Chromate and Aniline respectively. The weight losses of Aluminium were also lower than that witnessed in cold steel.



Figure 1: Plot of weight loss against the time for the exposure of cold rolled steel to HCL corrosive medium in the presence 2 g/L and 11 g/L K2CrO4and C6H5.NH2 corrosion inhibitors

Figure 2: Plot of weight loss against the time for the exposure of Aluminium to HCl corrosive medium in the presence of 2 g/L and 11 g/L of (a) K2CrO4 (b) C6H5.NH2 corrosion inhibitors

This can be seen in Figure 1, in the plot of the weight losses against the exposure time in the HCl solution in the presence of various concentrations of Potassium Chromate and Aniline inhibitors.

The rate of weight loss experienced with the Aluminium were lower compared to that obtained in cold steel due its tendency to form a thin protective oxide layer (Al2O3) when exposed to air (Zhang *et al*., 2019; Pan *et al*., 2024). As much as the oxidation reaction in (2) is the basis of the corrosion in HCl, there is a competing reaction of the HCl corrosion medium with the protective oxide layer, which makes the weight losses experienced with the Aluminium much lesser than that of the cold rolled steel.

**3.2.2 Corrosion Rate (CR)**

The reduction in the Corrosion Rate was used as a metric in measuring the effectiveness of corrosion control method. This is a measure of how much corrosion is mitigated over time and also a direct indicator of the inhibitors’ preventative impact. The results indicated that the corrosion rate (CR), in the presence of different concentrations of the K2CrO4, varied considerably for the cold steel and aluminium samples as shown in Tables 1-4. It was found that the corrosion rates were lower in 11g/L than in 2g/L concentration of K2CrO4. Equally, samples of the cold steel and aluminum exposed to the HCl acidic medium in the presence of various concentrations of C6H5.NH2as inhibitor showed similar reduction in the corrosion rates. In the case of cold rolled steel, C6H5.NH2was more effective as an inhibitor when compared to K2CrO4 especially at higher concentrations. However, the corrosion rates were comparable, for both K2CrO4and C6H5.NH2in the case of aluminium samples irrespective of their concentrations. The corrosion rates were also found to reduce as the duration increased from 24 hours to 72 hours.

**3.2.3 Inhibitor Efficiency, I.EM (%)**

The results for the inhibitor efficiency (I.EM (%) measurements for 0.5M HCl with K2CrO4 and C6H5.NH2as shown in Figures 3 and 4 respectively. Based on the chemical interactions between the metals and the inhibitors in the acid medium, better inhibitor efficiency was noted at the higher concentration of K2CrO4 and C6H5.NH2 inhibitors, for the cold steel and aluminium metals respectively.



Figure 3: Plot of inhibition efficiency (% I.EM) against the time for the exposure of cold steel to HCl corrosive medium in the presence of 2 g/L and 11 g/L of (a) K2CrO4 (b) C6H5.NH2 corrosion inhibitors



Figure 4: Plot of inhibition efficiency (% I.EM) against the time for the exposure of Aluminium to HCl corrosive medium in the presence of 2 g/L and 11 g/L of (a) K2CrO4 (b) C6H5.NH2corrosion inhibitors

The highest inhibition efficiency (85.96 %) was recorded for K2CrO4 at 11g/L after 72 hours of inhibition, whereas, the least inhibitor efficiency that was recorded for K2CrO4 was (37.90 %) at 2g/L for the cold steel samples.

In the case of Aluminum, the highest inhibition efficiency (84.76 %) was recorded for K2CrO4 at 11g/L after 72 hours of inhibition, whereas, the least inhibitor efficiency that was recorded for K2CrO4 was (37.90 %) at 2g/L. Also, marked inhibition of the corrosion of Aluminium was witnessed when C6H5.NH2was applied at various concentrations. A maximum inhibition efficiency of 96.13 % after 72 hours of exposure to the acidic medium containing 11 g/L of the inhibitor. The inhibition efficiency thus increased with inhibition time and inhibitor concentration for both inhibitors and for both metals. The variation of the inhibition efficiencies with time for the various concentrations of the inhibitors depends strictly on the rate of the adsorption of the molecules of the inhibitor on the samples surfaces, in order to counteract anodic and corrosive reactions.

The parameters of corrosion obtained from the weight loss method of cold rolled steel in an acidic solution in the presence of various concentrations of corrosion inhibitors indicate that the percentage I.EM (%) increases and (CR) values decrease with inhibitor concentration. This is because the inhibitor’s concentration increase the amount of the inhibitor that adsorbs on the mild steel surface (Mahdi *et al.,* 2022). Also, the cold rolling of the steel as a part of the production process introduces dislocations and strains into the microstructure of the steels. These dislocations and strains resulted in a higher surface energy compared to other types of steels and also aluminum (Hossein and Roohollah, 2024).

To this end, the higher rates of weight loss and corrosion observed in the cold rolled steel as compared to the aluminium, beyond the Al2O3 protective layer found on the aluminium, is due to this factor. The corrosion inhibition is therefore due to the adsorption of the complexes formed by the$CrO\_{4}^{2-}$ions with Fe2+ and Al3+ ions on the surfaces of the cold rolled steel and aluminium, respectively. Considering the aniline inhibition, the inhibitive process is expected to be different from that exhibited by the Potassium Dichromate inhibitor. In this case, the reaction center through which an adsorption complex if formed on the surfaces of the cold rolled steel and aluminium is on the nitrogen atom (Liu *et al*., 2025). The high electron density on the Nitrogen atom is useful in the formation of monolayer of the inhibitor by a reaction with Fe2+ and Al3+ ions on the surfaces of the cold rolled steel and aluminium, respectively.

The organic corrosion inhibitors indicated higher efficiencies when applied in a high concentration to inhibit the metal surface from a corrosive medium. Organic inhibitors are well known for their adsorptive properties (site-blocking elements), enabling the active molecules to adsorb on exposed metal surfaces. The lower rate of corrosion at these higher concentrations of the inhibitors is therefore due to a higher rate of the adsorption process on the metal surface, which can be affected by either the anodic or cathodic reaction kinetics and the rate of diffusion of aggressive ions from the metal surface (Krishnaveni and Ravichandran, 2014).

The K2CrO4 and C6H5.NH2 inhibitors used consist of oxygen and nitrogen atoms respectively, through which they have demonstrated an intrinsic capability to form a protective layer between the metal surfaces and corrosive environment through the adsorption process to slow down the metal disintegration (Al-Amiery *et al.*, 2023; Goyal *et al*, 2018; Verma *et al*, 2016; Mobin *et al*, 2019; Tamalmani and Husin, 2020). The nitrogen and oxygen atoms donated their lone electrons pairs to the metal surfaces resulting in chemisorption on the metal surface (Shwetha *et al.*, 2024).

4. Conclusion

Corrosion is a primary cause of the degradation and a principal threat to industrial and national infrastructure. The infrastructure replacement cost is a major driver on the economic impact of corrosion and can increase if corrosion preventive strategies are not adequately applied. The problems associated with the impact of corrosion on industrial chemical environments usually found in the petroleum and allied chemical industries can be mitigated through preventative measures to inhibit the metal surface from corroding. This investigation evaluated the interfacial behavior and performance of the metals in the presence of inorganic and organic inhibitors, through the metal-inhibitor-media interaction mechanism. It can be concluded that weight loss data can be used to evaluate the inhibitor effect on corrosion of metals. The inhibitor efficiencies (I.EM %) measurement results varied considerably in the presence of K2CrO4 and C6H5.NH2 in the HCl acid medium. There was better inhibition efficiency in the higher concentration than in the lower concentration of the inhibitors. The inhibitors impacted the anodic metallic dissolution and the cathodic hydrogen evolution reactions. The results obtained indicated the effectiveness of the inhibitors in minimizing metallic corrosion when compared to the uninhibited (control) solutions. It can also be concluded that the organic corrosion inhibitor (aniline) indicated better performance than the inorganic inhibitor (potassium chromate). However, the type of inhibitor that is most appropriate when considering mitigation depends on the specific application, the severity of the corrosion environment, and the desired level of efficacy. Therefore, the extent of corrosiveness of the environment and desired level of effectiveness will altogether influence the type of inhibitor that is utilized.

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