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JOURNAL OF PURE AND APPLIED SCIENCES

CORROSION BEHAVIOUR OF MILD STEEL IN HYDROCHLORIC AND SULFURIC ACIDS

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ABSTRACT
The corrosion behavior of mild steel in hydrochloric and sulfuric acids was examined using the weight loss method. The findings indicated that both weight loss and corrosion rate rose with higher acid concentrations and temperatures. Specifically, the corrosion rates for hydrochloric and sulfuric acids at 0.5M, 343 K, and over 5 hours were 0.01012, 0.01267, and 0.00805 g/cm²/hr, and 0.01450, 0.01950, and 0.01450 g/cm²/hr, respectively. The enthalpy change values for HCl and H_2SO_4 indicated that the corrosion reactions between these acids and mild steel were endothermic. Specific values of 15.168 and 20.040 kJ/mol provide insights into the energy changes occurring during the corrosion process. Sulfuric acid has a higher corrosion rate for mild steel than other acids, despite the difference in activation energy.

Keywords: Corrosion Rate, HCl, H_2SO_4, Mild Steel, Weight loss

INTRODUCTION

Mild steel is a low carbon steel type. Carbon steels are metals with a small amount of carbon (up to 2.1%) that improves the properties of pure iron. The carbon content varies according to the steel's specifications. Carbon content in low carbon steels ranges between 0.05 and 0.25 percent. Mild steel is available in a variety of grades. However, their carbon content is all within the above-mentioned limits. Other elements are incorporated to improve useful properties such as corrosion resistance, wear resistance, and tensile strength (Adreas, 2020). Despite its many technical applications, structural steel's usefulness is constrained by its poor corrosion resistance in acidic environments. Hydrochloric and sulfuric acid solutions are primarily used in industrial processes such as acid pickling, acid descaling, industrial cleaning, and oil-well acidizing. In aqueous acidic solutions, metals and alloys develop a highly protective oxyhydroxide passive film on their surface, which influences their corrosion behavior (Singh and Ray, 2007). The corrosion behavior of carbon steel in acidic solutions is crucial due to its extensive use, particularly in the production of pipelines for the petroleum industry. Acidic solutions are frequently employed to eliminate rust and scale that accumulate during industrial processes (Greene *et al*., 1961). Furthermore, mild steel has low natural stability and degrades significantly in mineral acid environments like HCl and HNO_3 (Katerina *et al*., 2013). Corrosion is a natural process that converts metals into more stable oxides. It involves the slow deterioration of materials, typically metals, due to chemical reactions with their environment (Breakell, 2015). In its most common usage, this term refers to the electrochemical oxidation of a metal when it reacts with an oxidant, such as oxygen. A familiar example of electrochemical corrosion is the formation of iron oxides during rusting. This process typically produces oxides or salts of the original metal, characterized by a distinct orange coloration. While corrosion can also affect materials like ceramics or polymers, the term "degradation" is more commonly applied in these contexts. Corrosion deteriorates the useful properties of materials and structures, including strength, appearance, and permeability to liquids and gases (Breakell, 2015). Structural alloys often corrode when exposed to atmospheric moisture, though this process can be significantly affected by specific substances. Corrosion may manifest locally, creating pits or cracks, or it can spread uniformly across larger surfaces. It occurs on exposed surfaces due to being a diffusion-controlled phenomenon. Techniques like passivation and chromate conversion, which decrease the reactivity of exposed surfaces, can enhance the corrosion resistance of materials. However, certain corrosion mechanisms are more subtle and harder to foresee. Corrosion refers to the deterioration of metal and its characteristics due to chemical (dry corrosion) or electrochemical (wet corrosion) reactions with its surroundings. The current definition excludes nonmetals (Breakell, 2015). Thus, the objective of this study is to assess the corrosion behavior of mild steel in hydrochloric acid and sulfuric acid.

MATERIALS AND METHOD

Preparation of Mild Steel Coupons

The sheets were pressed and cut during the preparation of mild steel coupons sourced from Sharada Market in Kano State, Nigeria, resulting in dimensions of 2 x 2 x 0.1 cm. In order to achieve the desired finish, the coupons underwent thorough polishing using different grades of emery paper. They were degreased with ethanol, dried with acetone, and stored in a desiccator until needed.

Preparation of Solutions

Double-distilled water was used to prepare stock solutions of analytical-grade hydrochloric acid (36.5%, 1.18 g/L) and sulfuric acid (98%, 1.84 g/L). Dilutions were used to prepare acidic solutions with concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5M (Husaini *et al.*, 2018).

Weight Loss Determination

Mild Steel coupons were weighted (W_1) and completely suspended in 0.5, 1.0, 1.5, 2.0 and 2.5M solutions of hydrochloric and sulfuric acids in a 250ml beaker during the weight loss experiments. The solution volume remained consistent at 50 ml. After 1, 2, 3, 4, and 5 hours, the coupons were removed, rinsed with distilled water, dried using acetone, and then re-weighed (W2).

Weight loss and corrosion rate were determined using the formula described in Equation 1-2.

$$W1 - W2 = \Delta W \quad (1)$$

$$CR = \frac{\Delta W}{AT} \quad (2)$$

Where: CR = Corrosion Rate (g/cm^2hr)
ΔW = Weight loss (g)
A = Area of Mild Steel (cm^2)
T = Time (hr) (Yahaya *et al.*, 2018).

Table 1: Result of the elemental analysis of the used mild steel

Elements	Percentage %
Fe	68.82
O	28.19
Si	0.69
Mn	0.51
Al	0.40
K	0.30
Cr	0.23
Cu	0.22
Co	0.16
Cd	0.14
Ni	0.12
C	0.08

RESULTS AND DISCUSSION

Results

The findings from the elemental analysis of the used mild steel, as well as the activation energy, thermodynamic parameters and the changes in corrosion rate with different concentrations, immersion times and temperatures during the evaluation of mild steel corrosion in HCl and H_2SO_4, are presented below:

Figure.1. show the effect and variation of various concentrations of hydrochloric and sulfuric acids on mild steel, indicating that both the weight loss and corrosion rate rose with higher acid concentrations. At the lowest concentration of 0.5M, the weight loss and corrosion rate of mild steel in HCl and H_2SO_4 were (0.027 and 0.031) g and (0.0450 and 0.00517) g/cm²/hr, respectively. At the highest concentration of 2.5M, these values increased to (0.057 and 0.087) g and (0.00950 and 0.01450) g/cm²/hr, respectively.

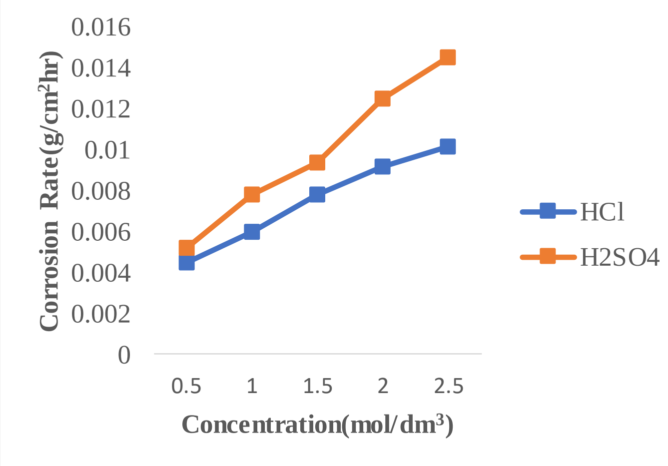

Figure 1: Changes in corrosion rate with different concentrations of HCl and H_2SO_4 for mild steel corrosion.

Results from Figure 2 illustrate how immersion time impacts weight loss and demonstrates the increasing corrosion rate of mild steel in HCl and H_2SO_4 with longer immersion durations. At a minimum immersion time of 1 hour, the weight loss and corrosion rate for HCl and H_2SO_4 are (0.023 and 0.038) g and (0.00575 and 0.00950) g/cm²/hr, respectively. At a maximum immersion time of 5 hours, these values increased to (0.161 and 0.290) g and (0.00805 and 0.01450) g/cm²/hr, respectively. The greater weight loss observed with longer immersion times results from the ongoing interaction between the acid and the metal surface in the solution. This interaction gradually deteriorates the metal surface over time, leading to increased metal weight loss. Specifically, at a constant concentration of the corrosive substance, the weight loss increases proportionally with the immersion time.

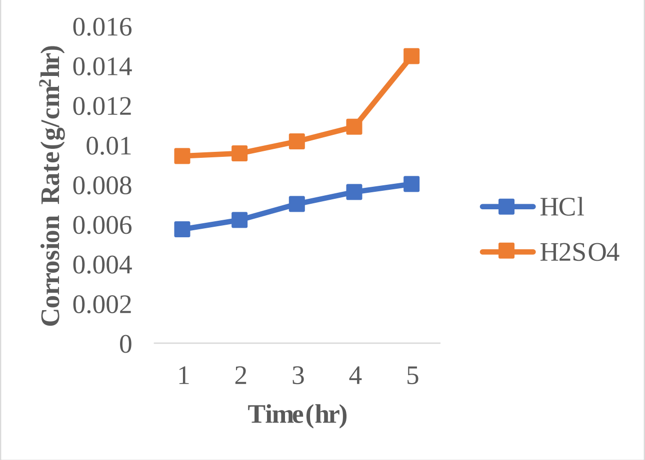

Figure 2: Changes in corrosion rate with different immersion times in HCl and H_2SO_4 for mild steel corrosion.

Figure 3 illustrates that corrosion rates increased with higher temperatures. Elevated temperatures lead to more severe corrosion. At the lowest temperature tested (303 K), the weight loss and corrosion rate of mild steel in HCl and H_2SO_4 were (0.033 and 0.041) g and (0.00550 and 0.00683) g/cm²/hr, respectively. As the temperature was raised to 328 K, the weight loss and corrosion rate increased to (0.076 and 0.17) g and (0.01267 and 0.01950) g/cm²/hr, respectively.

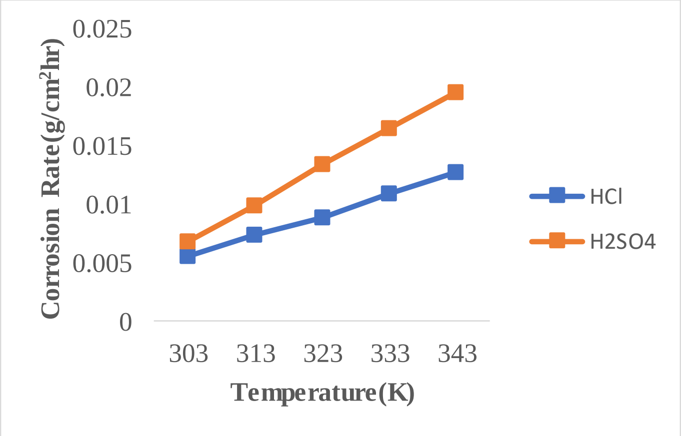

Figure 3: Changes in corrosion rate with different temperatures in HCl and H_2SO_4 for the corrosion of mild steel.

Table 2 and Figures 4-7 present the results of the apparent activation energies (Ea) calculated using the Arrhenius equation, along with the thermodynamic parameters such as enthalpy and entropy of activation, which were determined using equation 3 from Husaini *et al*., (2018).

$$ln(CR) = B - \frac{Ea}{RT} \quad (3)$$

In this equation: B represents a constant, R represents the universal gas constant, and T represents the absolute temperature. When plotting ln(CR) against the reciprocal of absolute temperature (1/T), a straight line was obtained with a slope of -Ea/R. This slope was used to calculate the activation energy values for the corrosion process.

$$\ln\left(\frac{C_R}{T}\right) = ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_a}{R}\right) - \left(\frac{\Delta H_a}{RT}\right) \quad (4)$$

Where h represents Planck's constant and N denotes Avogadro's number. A graph of $\ln\left(\frac{C_R}{T}\right)$ against $\frac{1}{T}$ produced a straight line with a slope of slope $= -\left(\frac{\Delta H_a}{R}\right)$ and an intercept of $ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_a}{R}\right)$.

Activation energy is the least amount of energy needed for a chemical reaction to occur. Higher activation energy indicates that the corrosion process in sulfuric acid demands more energy to progress than in hydrochloric acid. Several factors such as acid concentration, oxidizing ability and acid strength can contribute to sulfuric acid having a higher corrosion rate for mild steel compared to hydrochloric acid, despite the difference in activation energy.

The change in enthalpy values for HCl and H_2SO_4 indicate that the corrosion reactions between these acids and mild steel are endothermic. The specific values, 15.168kJ/mol for HCl and 20.040 kJ/mol for H_2SO_4, provide insights into the energy changes occurring during the corrosion process.

Table 2: Activation energy and thermodynamic parameters for the corrosion rate of Mild Steel HCl and H_2SO_4

Acids (mol/dm3)	Activation Energy (Ea) (kJ/mol)	Enthalpy (kJ/mol)	Entropy (J/molK)	ΔG (kJ/molK)	R_1^2	R_2^2
HCl	17.846	15.168	−157.082	47613.692	0.9943	0.9917
H_2SO_4	22.717	20.040	−175.145	53091.652	0.9858	0.9812

The change in entropy (ΔS) values for HCl (-157.082 J/molK) and H_2SO_4 (-175.145 J/molK) indicate **a decrease in disorder or an increase in order** during the corrosion process. These highly negative values suggest the formation of more structured interactions between the mild steel surface and the corrosive environment, possibly due to the deposition of corrosion products or the stabilization of intermediates. The more negative ΔS value for H_2SO_4 (-175.145 J/molK) implies a greater increase in order during corrosion compared to HCl. This higher degree of order may correspond to the formation of more stable surface layers, potentially reducing the overall corrosion rate despite the system becoming more ordered. Other factors, such as activation energy and enthalpy, must also be considered to fully understand the corrosion behavior in these acids.

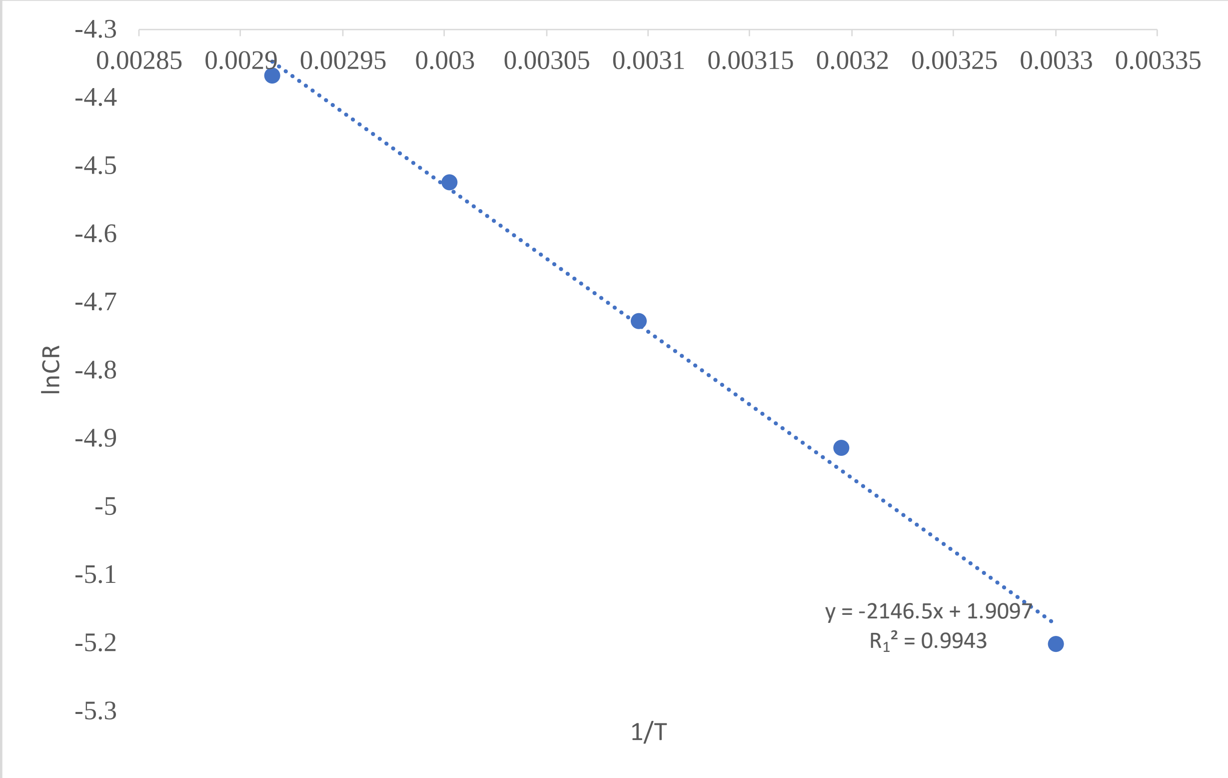

Figure 4: Variation of ln(CR) with 1/T for the corrosion of mild steel in HCl.

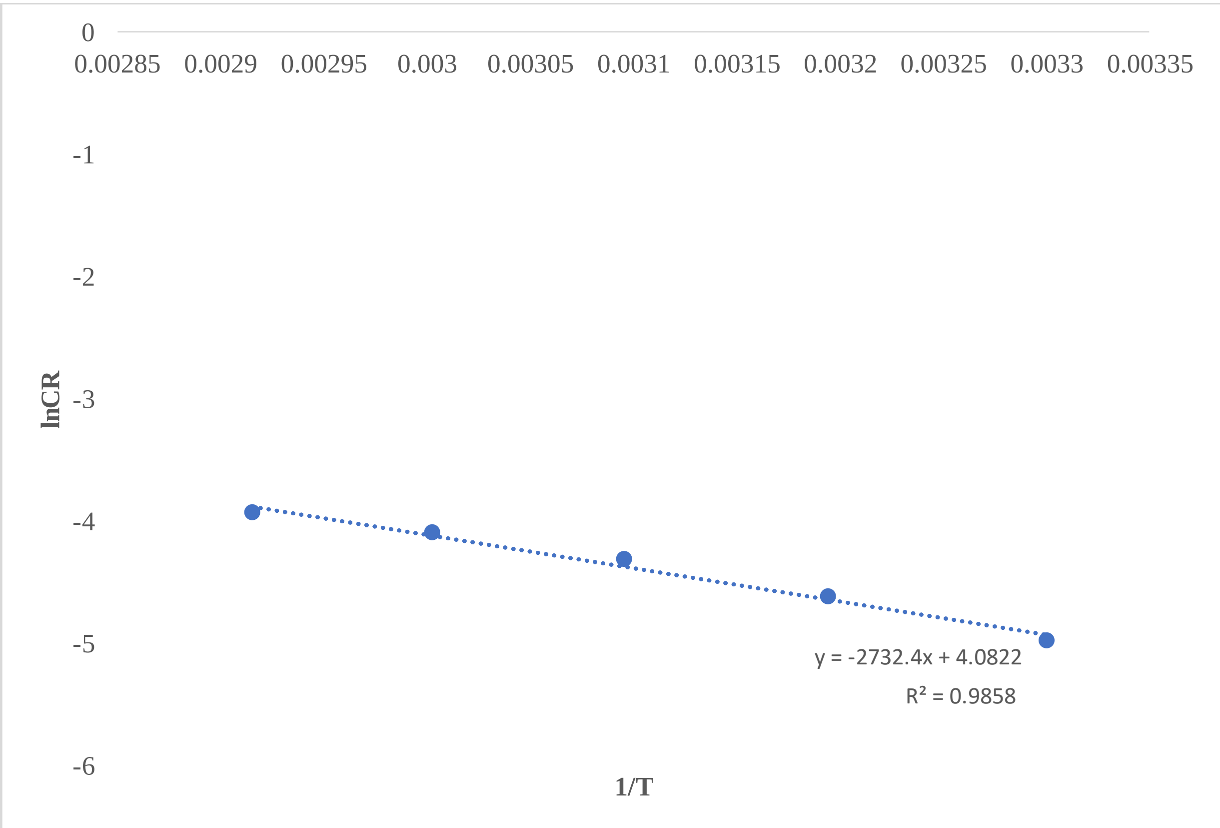

Figure 5: Variation of ln(CR) with 1/T for the corrosion of mild steel in H_2SO_4.

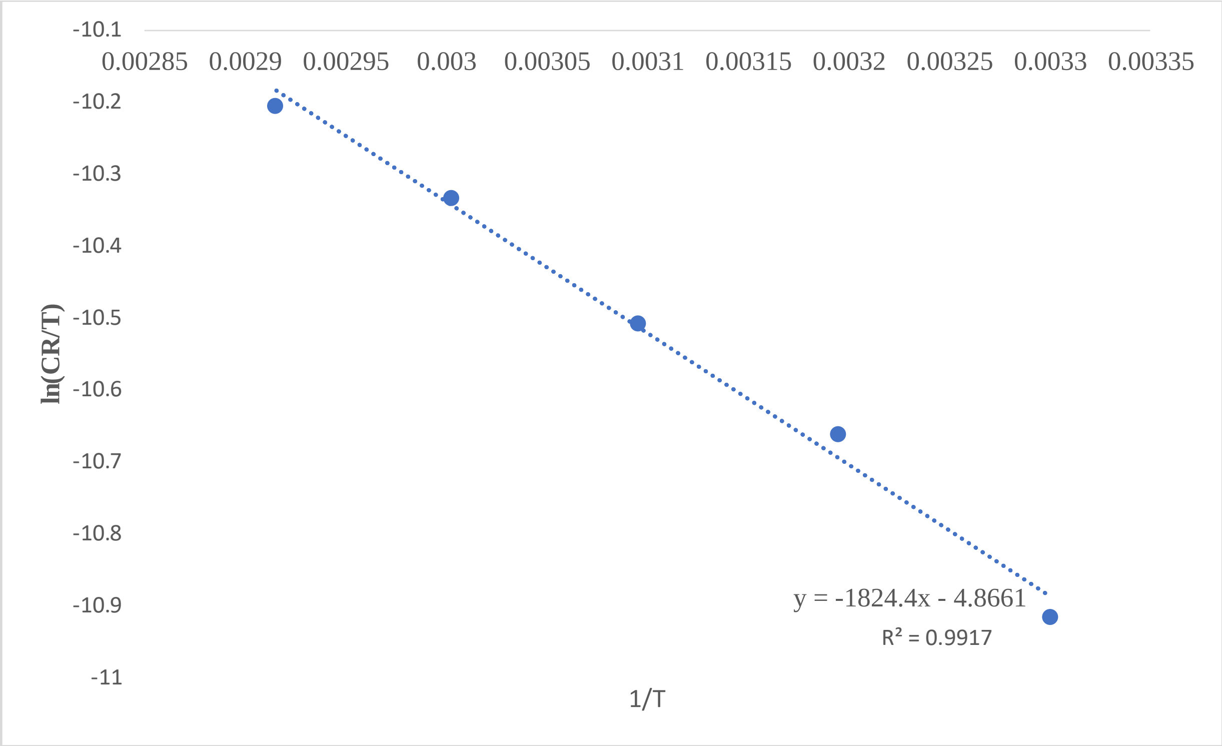

Figure 6: Variation of ln(CR/T) with 1/T for the corrosion of mild steel in HCl.

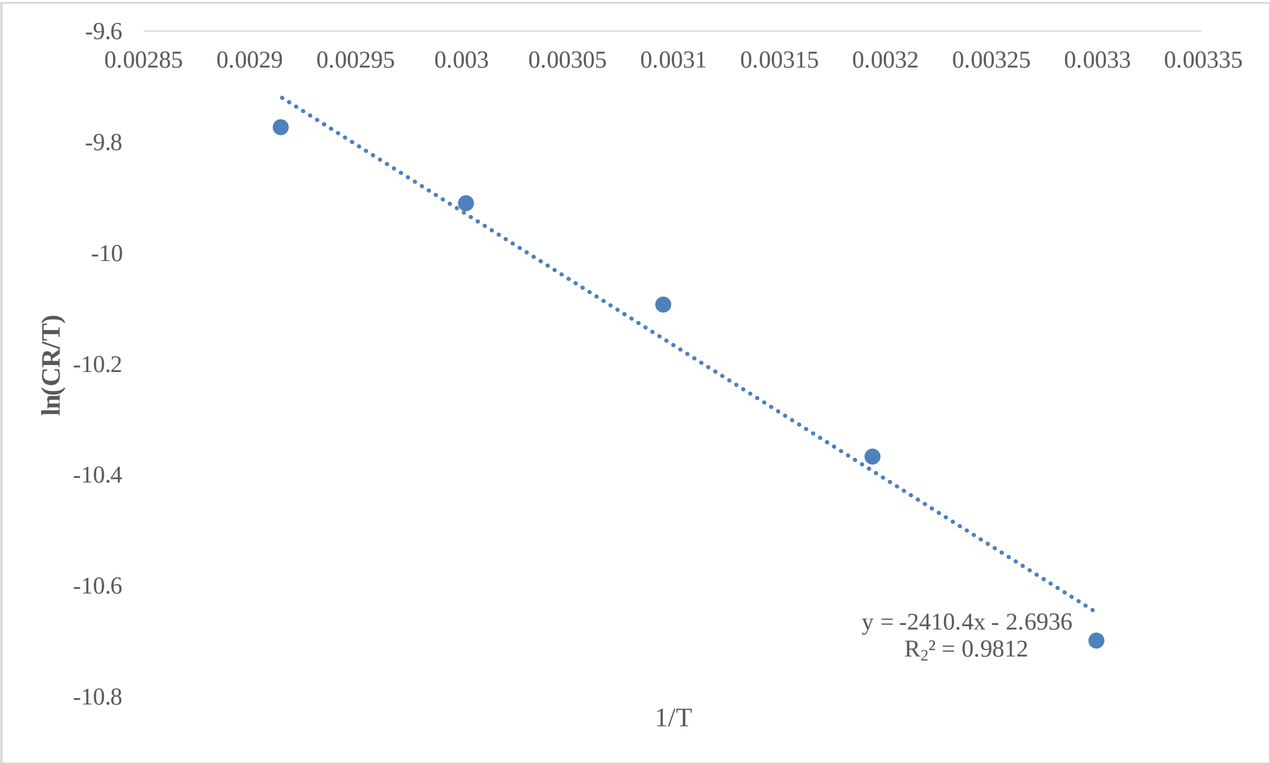

Figure 7: Variation of ln(CR/T) with 1/T for the corrosion of mild steel in H_2SO_4.

CONCLUSION

The findings reveal that as immersion time increases in various acid environments, weight loss also increases. Additionally, the corrosion rate rises with higher concentrations and temperatures in both acids. Comparing mild steel's corrosion rates in the two different acid environments demonstrates that sulfuric acid is more corrosive than hydrochloric acid. This disparity is influenced by sulfuric acid's concentration, strength, oxidizing capacity, and the passivating effects of hydrochloric acid, which forms a protective barrier against continued corrosion.

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