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1. Introduction

A corrosion process can be influenced, in different ways, by the relative movement between the metal and the corroding environment.

Researchers pay close attention to carbon steel because of its many practical applications (Li et al, 2022; Hasan and Sadek, 2014).

The primarily effects on corrosion rate by velocity where its influence on

diffusion phenomena and slight effect on activation controlled processes (Poulson, 1983).

Sulfuric acid is a common component in the chemical industry. Its widespread use is in petroleum industry, fertilizer , mineral processing, oil refining, wastewater processing, chemical synthesis, steel pickling, etc. (Muller et al, 2000). The acids aggressive character, on the other hand, causes it to damage the metallic materials used in storage tanks and pipe construction. As a result , a wide range of metallic materials are used for constructing tanks and pipes depending on the concentration range of sulfuric acid (Panossian et al, 2012). The corrosion behavior of carbon steel in sulfuric acidic solution is noteworthy

Abstract

The impact of flow velocity (0-900 rpm) on the corrosion rate of carbon steel in a wide range of sulfuric acid concentrations (0-90% in H2O) at 30 °C and 1 h was studied and discussed. In addition, the efficiency of corrosion inhibitor (dimethyl disulfide, DMD) was evaluated in hardest corrosion conditions for the range of velocity investigated. The results revealed that increasing the flow velocity of H2SO4 solution, increases the corrosion rate depending on the acid concentration. When the flow velocity is increased of H2SO4 solution, the corrosion potential was shifted to more negative. The DMD inhibitors showed significant inhibition efficiency at high velocities, where the highest percentage of inhibitor efficiency reached 98% at 900 rpm.

Keywords: Corrosion Rate, Carbon Steel, Sulfuric Acid, Flow Velocity, Inhibitor.

تأثير سرعة التدفق على تأكل الصلب الكربوني وتخفيف تآكله في نطاق واسع من تركيز حامض الكبريتيك مما حسين كاظم، باسم عبيد حسن، ساهر الزريجي، حسين زناد الخلاصة:

تمت دراسة ومناقشة تأثير سرعة التدفق (٠-٠٠ دورة في الدقيقة) على معدل تآكل الفولاذ الكربوني في نطاق واسع من تركيزات حامض الكبريتيك (٠-٩٠٪ في (H2O عند ٣٠ درجة مئوية و ١ ساعة. بالإضافة إلى ذلك ، تم تقييم كفاءة مثبط التآكل (ثنائي ميثيل ثاني كبريتيد ، (DMDفي أصعب ظروف التآكل لنطاق السرعة التي تم فحصها. أظهرت النتائج أن زيادة سرعة تدفق محلول حامض الكبريتيك يزيد من معدل التآكل اعتمادًا على تركيز الحمض. عندما تزداد سرعة التدفق لمحلول لماكل ، تحولت احتالية التآكل إلى سالب أكثر. أظهرت مثبطات DMD كفاءة تثبيط معنوية عند السرعات العالية حيث بلغت أعلى نسبة كفاءة للمثبط ٩٨٪ عند ٠٩ دورة في الدقيقة

> due to its broad uses, namely in manufacturing pipelines for the petroleum industries. It is commonly utilized in removing rust and scale-developed industrial processes. (Greene et al, 1961).

> The corrosion reactions of iron in sulfuric acid include iron oxidation reaction:

$$\begin{array}{ccc} Fe & \longrightarrow & Fe^{2+} + 2e & (1) \\ \text{and the cathodic reduction reaction of hydrogen} \\ & 2H^+ + 2e^- & \longrightarrow & H_2 & (2) \end{array}$$

When concentrated sulfuric acid comes into contact with carbon steel, the former is converted to produce H_{τ} , and the iron oxidizes to produce ferrous sulfate (FeSO₄), as in the following reaction [Panossianet al, 2012]:

 $H_{r}SO_4 + Fe \longrightarrow FeSO_4 + H_2$ (3)

Metals exposed to corrosive environments are greatly affected by the relative velocity between the fluid and the metal surface, especially those metals that create a protective coating or have passive behavior (Abood et al, 2008). Oxidizer is rapidly distributed by means of turbulence through the fluid bulk, but has

NJES is an open access Journal with ISSN 2521-9154 and eISSN 2521-9162 This work is licensed under a <u>Creative Commons Attribution-NonCommercial 4.0 International License</u> more difficulty diffusing through the laminar region to reach the metallic surface.

Dimethyl disulfide (DMDS) is an active sulfur compound of high sulfur content (68%), and its decomposition temperature range is 360-450°F (182-232°C) (Sharifi-Asl et al, 2017). The mechanism of inhibition can be understanding depended on different factors such as chemical structure, functional groups, the interaction between the surface of metal and inhibitor, inhibitor adsorption process, and other physical and chemical properties.

Due to the flow impacts on both cathodic and anodic processes, velocity of the fluid is one of the most important critical elements to consider during metal corrosion. (Musa et al, 2011). The effect of velocity on the rate of corrosion is complicated and depends on the characteristics of the metal as well as the environment to which it is subjected. The impact of flow velocity on the corrosion rate of metals in acid solution is still needing further study and discussion. The effect of hydrodynamics on the corrosion rate is intricate by the contribution of different factors such as the mass transfer rate of oxidizing species, the thickness of the diffusion layer, the surface roughness, and the surface electrochemical behavior. Understanding the conjoint effect of this parameter is important for characterizing the corrosion behavior for the final target of suggesting corrosion mitigation method for the specified condition.

In many corrosion problems, there is potent evidence that the mass transfer rate controls uniform corrosion rate. This is true whether the corrosive fluid is constant or moving quickly across the metal surface. However, in acids corrosion the kinetic of corrosion reaction is also influential which are dependent of the nature of both cathodic and anodic behavior.

Ciubotariu et al, [2010] found that the rate of corrosion in 0.5M H2SO4 is higher than 0.5M NaCl solution because the corrosion resistance in acid declines over time due to the dissolution of corrosion products in contrast to 0.5M NaCl solutions where the corrosion resistance increases with time due to the accumulation of corrosion product layer.

Musa et al, [2011] determined the rate of corrosion for mild steel in 2.5 M H_2SO_4 at 30 °C for different flow velocities. Electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and Tafel polarization were carried out to study the effects of flow velocity on rate of corrosion mild steel. The experiments of turbulent conditions were simulated using rotating cylinder electrode (RCE). The results show that the corrosion rate of mild steel decreased with increases in flow velocity due to improvement of the passivation by an increase of the oxygen supply. Corrosion potentials were shafted toward the cathodic values and the magnitude of the impedance was rose with flow velocities.

Hasan and Sadek, [2014] investigated the corrosion of carbon steel in hydrochloric acid (HCl)-sodium sulphate (Na2SO4) solution mixture using rotating cylinder electrode (RCE) for a range of rotation velocity, 0–2000 rpm, solution temperature of 32–52 °C, and different oxygen concentrations. The corrosion rat was determined by using both weight



method and electrochemical polarization loss technique. Different acid and salt concentrations were used ranged from 0.01 to 0.2 M for salt and 0.5 to 5% for acid. The effects of operating conditions on indole and cetyl trimethyl ammonium bromides (CTAB) inhibition efficiency were also studied. The results showed that increasing the rotational velocity leads to an increase in the corrosion rate depending on the concentration of salt and acid. Increasing the temperature and acid concentrations leads to an increase in the corrosion rate while the corrosion rate exhibited unstable trend with salt. The inhibition efficiency of the used inhibitors was found to decrease with increasing velocity. In addition, indole inhibitor reveals excellent inhibition efficiency even at high temperatures while CTAB efficiency decreased appreciably with temperature increase.

Hussein et al. [2016] reported that the corrosion rate of carbon steel in 5% H₂SO₄ is significantly increased with, increasing rotational velocity.

Studies concerning the corrosion behavior in H₂SO₄ solution under flow conditions are limited in open literature. The objective of his work is to investigate the influence of flow velocity on the corrosion rate of carbon steel in a range of sulfuric acid concentration (0-90%). It is aimed also to examine the efficiency of corrosion inhibitor (dimethyl disulfide) in this range of concentration under flow conditions.

2. Experimental Work

Figure 1 presents the experimental setup which comprised water bath having a temperature range from 10 to 95 °C used to obtain different solution temperatures, saturated calomel electrode (SCE) connected to voltmeter for corrosion potential measurement. A mechanical stirrer (Stuart, UK) equipped with 4-blades impeller (Rushton turbine) was used to obtain the desired rotational velocity. A sheet of carbon steel specimen was machined and fixed on specimen holder in the solution. The specimen dimensions 40 mm \times 40 mm \times 0.5 mm exposed to the corrosive environment.

Before each test, the electrode specimen was abraded using glass emery paper with grade numbers 120, 180, 220, 400, and 2000, cleaned with a plastic brush in running tap water, followed by distilled water, dried with a clean tissue, and then immersed in ethanol for 30 minutes. Then, the specimen was dried in the electrical oven at about 80 °C for 3 minutes. The specimen was then placed in a vacuum desiccator on high-activity silica gel until it was ready for use. The specimen was then weighted (w1) to determine weight loss using a digital balance. After that, one face of the rectangular coupon was exposed to a corrosion environment, while the other face was completely insulated by insulating tape. After the weight loss experiment, the corrosion products on the surface were cleaned using a plastic brush, followed by rinsing the specimen with tap water, brushing it with distilled water, and drying with clean tissue. It was then kept in an electrical oven at a temperature of 80 °C for 3 minutes for further drying, and then weighed (w2). As a result, the corrosion rate may be calculated as follows:

CR (gmd) = W/At (1)

Where CR is the corrosion rate measured in gmd (gram/m².day), $W = w_1-w_2$, A is the specimen area, and t is time of exposure. Upon completion of the corrosion test, observation of microstructures and morphological analyses were done by using optical microscopy (OM).



Figure (1): Experimental setup for weight loss method.

3. Result and Discussion

3.1 Corrosion rate

Figure 2 presents the variation of corrosion rate of carbon steel (CS) with flow velocity in different H_2SO_4 concentrations. This figure shows that increasing the flow velocity causes and increase in the corrosion rate for all H_2SO_4 concentrations. The highest increase is for 20% and 30% H_2SO_4 concentration as indicated by best fit lines, while the lower concentrations the effect is less.

The increase in the corrosion rate with flow velocity is ascribed to the increased turbulent transport, which enhances the transport of O_2 to the metal surface. The rate of the oxygen reduction reaction is restricted by how quickly oxygen can reach the metal's surface. Previous studies {Foroulis et al, 1979; Scheers et al, 1992; Slaiman and Hasan, 2010; Fiala et al, 2019; Suwarno and Nashir, 2020] indicated that high velocities cause increased turbulence, which results in higher O_2 concentrations near the surface.

Earlier studies confirmed (Turkee et al, 2009; Hasan and Sadek 2014; Fiala et al, 2019; Suwarno and Nashir, 2020) that demonstrated that the rate of corrosion in acidic environments liquids increases with the flow. The higher the flow velocity, the higher the oxygen arrival to the surafce, (Hussein et al, 2016; Hasan and Sadek 2013; Hussein et al, 2018). Furthermore, it can be observed that at high flow velocity, the corrosion rate at a high concentration of H₂SO₄ (90%vol) is lower than that at a low concentration. This is attributed to the fact when the layer of corrosion product (FeSO₄) becomes relatively thick and sticky to the surface of the steel, it creates a barrier to protect the steel. This results in a reduction in the corrosion rate epically for high H2SO4 concentrations (Panossian et al, 2012)

It can be seen from Fig. 2 that the effect of flow velcity on the corrosion rate is more pronounced for 20% and 30% concentrations as the line slope is highest 8.7 and 6.8 as indicated by the best fitting equation presented on the figure. For 20% H_2SO_4



when the velocity increases from 0 to 900 rpm, the corrosion rate increases by up to 1.5 times. This behavior is ascribed to the fact that when the concentration of sulfuric acid increases the oxygen solubility decreases. This reduces the influence of velocity on the corrosion rate, as the oxygen corrosion is mass transfer control. Additionally, the thickness of formed oxide protective layer increases with increasing flow velocity reducing the effect of flow on the corrosion rate.

With the increase in the fluid flow velocity, the thickness of the laminar region becomes thinner and, thus, there is an acceleration in the rate at which oxidant is brought to the surface of the metal. At high speeds, mechanical effects appear which increases the damage to the corroded metal (Slaimana and Hasan, 2010). When the erosion removes the protective layer or the scale film, the metal continues to corrode at a high rate.



Figure (2): Variation of Corrosion rate with flow velocity at different H₂SO₄ concentrations, T=30 °C.

second.			
U(rpm)	U(m/s)		
0	0		
300	0.393		
600	0.785		
900	1.178		

Figure 3 presents photos of clean and corroded specimens under different investigated conditions. It can be seen that the surface damage due to corrosion is increased with acid increasing oxygen concentration. A black corrosion deposits film is formed on the surface at 30% H₂SO₄ concentration due to the severity of corrosion.



Figure (3): carbon steel specimen (a) before corrosion, after (b) 5%, (c) 10%, and (d) 30% H₂SO₄ solution at 30 °C, 1h and 600 rpm.

Fig.4 shows the microscopic images of corroded specimens for different flow velocities values. Images a, b, and c show the sample's surface morphology after corrosion in 10%vol H₂SO₄ at different flow velocities. It is obvious that when velocity increases the surface damage increases especially at high velocity. Sample (c) displays extreme corrosion damage in that big pits begin to form and corrosion effect is clearly noticed.



Figure (4): Microscopic image of clean and corroded surface in 10% H₂SO₄, 1h (a) before corrosion at 0 rpm, (b) corroded at 300 rpm, (c) corroded at 600 rpm.

3.2 Corrosion Potential

As shown in Fig. 5 the trend of corrosion potential vs. exposure time at different velocities for 0.1N NaCl solution, i.e. no H₂SO₄. This figure is incorporated the show the difference in the corrosion behavior with the H₂SO₄ solution. With increasing time, the value of corrosion potential shifts to a more negative one. After 1 h, the corrosion potential becomes almost constant and the curve becomes linear for all the flow velocities. The reason for this decrease in the corrosion potential is due to the increase in the corrosion rate with time, which causes the increase in the thickness of the corrosion film on the metal surface. This film increases the electrical resistance and thus shifts (a) (b) (c) Page 13 of 22 the potential to more negative. In addition to this, this layer decreases the access of O₂ to the surface of the metal which also shits the potential to be more negative (Slaiman and Hasan, 2010; Hassan et al, 2011). When the flow rate is increased, the corrosion potential shifts to a more negative direction. This is because the formation of corrosion product layer (iron oxide) which is sticky leading to decrease the arrival of O₂ to the surface shifting the potential to negative as it increases the electrical resistance. (Foroulis, 1979;Hasan and Sadek 2014).





Figure (5): Variation of Corrosion potential vs. time for salt solution at T=30 °C, and different velocities.

Figures 6 to 8 display shows the trend of corrosion potential with time for different H_2SO_4 concentrations and different velocities namely 0, 300, 600, 900 rpm respectively. It is evident that for all flow velocities and all acid concentrations the corrosion potential shifts to more positive with time indicating that the severity of corrosion increases with time up to 60 min. This means the formed corrosion product layer is not able to restrain the corrosion and, thus, does not play a protective role as in case of salt solution shown in Fig. 5. This is true for 1 h exposure time; for longer time, the situation may change.

It can be seen from Figs. 6 to 8 that, in general, the corrosion potential shits to more negative with increasing flow velocity. The increased flow velocity causes an increase in the corrosion rate as in Fig. 2. This increases the formation of corrosion product layer and oxide fil on the surface leading to shift the potential to more negative.

Comparing Figs. 6 through 8 indicates that increasing H_2SO_4 concentration causes a shift of the corrosion potential to more positive. It can be seen that by an increase in the concentration of H_2SO_4 , the corrosion potential shit to more positive. This is ascribed to the increased hydrogen ion concentration, which enhances the corrosion (Hussein et al, 2016).



Figure (6): Corrosion potential vs. time at 5% H₂SO₄, T=30 °C and different velocities.



Figure (7): Corrosion potential vs. time at 10%vol H₂SO₄, T=30°C and different velocities.



Figure (8): Corrosion potential vs. time at 30%vol H₂SO₄, T=30°C and different velocities.

3.3 Efficiency of corrosion inhibitor

Figure 9 shows the corrosion rate of CS in H_2SO_4 solution with and without inhibitor when the velocity rate is increased from 0 to 900 rpm at 1h immersion time for inhibitor (DMD) concentration of 3.3 ppm. It can be seen that in the presence of inhibitor decreases the corrosion rate compared for the case of no inhibitor. When the velocity reaches 300 rpm, a sharp reduce in the corrosion rate is observed as in Fig. 9. This sharp decrease is thought to occur because of the conjoint effect of passivation and inhibitor action. This is consistent with the observation of Mohana et al [2013] who reported that flow is to effectively distribute the inhibitor (Mohana et al, 2013).

Table 2 lists the values of inhibition efficiency for different flow velocities in 30% H₂SO₄. The inhibition efficiency is excellent even at high flow velocity reaching to 98%. This indicates that DMD is successful corrosion inhibitor in sever corrosion conditions of sulfuric acid under flow conditions.

The increased flow velocity leads to increase oxygen transport to the metal surface causing more corrosion but in the presence of an inhibitor the curve down to a lower values because of adsorption of inhibitor molecules on the surface of the metal (Badiea and Mohana, 2009; Lopes-Sesenes et al, 2013). The inhibitor molecules form a passive layer at high flow velocity, which restrain the arrival of oxidant to the surface leading to a sharp reduction in the corrosion rate. Figure 10 shows that the corrosion potential in the presence of the inhibitor is more positive than blank case. Therefore, DMD is anodic inhibitor which form a protective layer on the surface shifting the potential to more negative. These inhibitors particularly alter the anodic reactions in a chemical cell, forcing the metallic surface into the passivation region.



Figure (9): Comparison of corrosion rate in the presence and absence of inhibitor for the investigated range of flow velocity.

Table (2): Inhibitor eff	ficiency with different flor	W
velocity at 30% H ₂ SO ₄ .	. 1h and 3.3 ppm of DMI).

Velocity(rpm)	CR(gmd) Without inhibitor	CR(gmd) With inhibitor	Inhibitor Efficacy%
0	15711	483	96.9
300	17403	1198.8	93.1
600	22053	345	98.4
900	21005	283.5	98.0



Figure (10): Corrosion potential vs. time in the presence of DMD corrosion inhibitor.

4. Conclusions

The results indicated that the carbon steel corrosion rate in the H_2SO_4 solution increases appreciably as the flow velocity. For the hardest corrosion conditions at 30% H_2SO_4 concentration, when the velocity increases from 0 to 900, the corrosion rate increases 1.5 times. In the H_2SO_4 solution, when the flow velocity increases, the corrosion potential shifts to more negative depending on the acid concentration. It was found that the corrosion rate at a high concentration of H_2SO_4 (above 30%vol) is lower than that at a low concentration for a wide range of flow velocity. In the presence of the inhibitor (dimethyl disulfide, DMD) when the velocity rate increases from 0 to 300 rpm, the corrosion rate also increases. Above this value of

NJES 27(1)91-96, 2024 Kazem et al.

velocity, the rate of corrosion starts to decrease appreciably and eventually approaches almost nil. The DMDS is an efficient cathodic corrosion inhibitor for all investigated range sulfuric acid concentrations. The inhibition efficiency of DMDS in 30% H₂SO₄ (the hardest corrosion concentration) is high even under flow conditions increased from (0-900) rpm reaching 98% indicating the effectiveness of this inhibitor.

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