

Improvement of 2-Acetylfuran as Corrosion Inhibitors of Mild Steel in Near Neutral and CO₂ Saturated Solution

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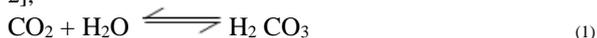
Abstract:

The use of corrosion inhibitors is crucial for protecting oil and gas facilities. Furan and its derivatives are under investigation and have been proven to be effective as corrosion inhibitors. In this work, furan derivative (2-Acetylfuran) was studied as a corrosion inhibitor to protect mild steel in a pH 5.5 solution saturated with CO₂. The results showed that a protection percentage of 92% can be achieved by 3 ppm of 2-Acetylfuran alone on mild steel. However, by adding 3 ppm of sodium thiosulfate pentahydrate to the solution, this percentage increases to 99.7%. At higher dosages of 2-Acetylfuran, the corrosion rate may increase due to the formation of acetic acid near the mild steel surface and increased hydrogen evolution. The increase in protection by the addition of sodium thiosulfate pentahydrate may be related to the formation of iron sulfide on the mild steel samples.

Keywords: Furan; polarization curve; linear polarization resistance; corrosion inhibitors

1. INTRODUCTION

One of the most critical problems facing oil and gas production is the issue of corrosion. Corrosion problems can occur anywhere in the production facilities, from the downhole equipment, production facilities, shipping lines, and refining equipment. The cost of lost time, the replacement of construction materials and the constant personnel involved in corrosion control are substantial; if not controlled, corrosion problems can be catastrophic. Carbon dioxide corrosion is one of the most prevalent forms of attack associated with oil and gas production. Carbon dioxide is a weakly acidic gas and becomes corrosive when dissolved in water. However, CO₂ must first hydrate to carbonic acid (H₂CO₃), which undergoes a relatively slow dissociation reaction, before it is acidic [1, 2],



It has been found that corrosion caused by carbonic acid solutions is more corrosive compared to strong acid solutions (completely dissociated acids) at the same pH, and the dissolution of CO₂ in water introduces two species which are potentially oxidizing [3], the hydrogen ion H⁺ and HCO₃⁻. Furthermore, the primary corrosion product is ferrous bicarbonate, a relatively soluble salt [4, 5]. Laboratories and on-site experiments have revealed that corrosion inhibitors are widely used as one of the most effective options to retard corrosion caused by CO₂ [6]. Recent studies have indicated that the failure of performance of corrosion inhibitors may be associated with different parameters, such as pH, material composition, flow rate, CO₂ partial pressure, and others. It is not easy to study and predict CO₂ corrosion under all these parameters. The majority of proposed CO₂ corrosion models are based on laboratory experiments, and the results of these experiments can be used to determine the feasibility of applying an inhibition treatment. The most commonly reported corrosion inhibitors are organic compounds containing heteroatoms, such as nitrogen, sulfur, oxygen, and phosphorus, as well as compounds with multiple bonds, which can facilitate the adsorption of inhibitors on the metal surface [7, 8]. Experimental and theoretical methods have been used

to investigate the corrosion inhibition efficiency of many organic compounds. The performance of organic inhibitors as corrosion inhibitors is related to the electronic structures of inhibiting molecules, steric factors, aromaticity, the density of electrons at the donor site, molecular area, and the molecular weight of the organic inhibitor. The interaction between the metal surface and the organic compound molecule increases with an increase in the number of lone pairs and π -electrons [9, 10]. Recently, inhibitors of single compounds are rarely used. At least two inhibitors are used in the final chemical formulation of corrosion inhibitors. This is because each inhibitor has its characteristic that allows it to work perfectly on a limited number of metals, a case that is not found in many systems. Additionally, corrosion inhibitors with multiple formulations can supplement their deficiencies with each other, thereby improving the mixed inhibitor efficiency and potentially reducing the dosage concentration, which in turn lowers the cost and the environmental impact of the chemical inhibitor [11]. Furan and its derivatives are heterocyclic organic compounds, consisting of a five-membered aromatic ring with four carbon atoms and one oxygen atom and the presence of two pairs of free electrons in their molecules. The characteristic increases the possibility of using them as effective corrosion inhibitors in many environments. Numerous previous studies have demonstrated the effectiveness of furan and its derivatives as corrosion inhibitors in various corrosion environments and conditions [12, 13]. On the other hand, acetic acid (HAc) is a weak organic acid that can be partially dissociated into hydrogen and acetate ions in the following chemical equation.



However, some studies have reported that HAc acts as a weak anodic inhibitor [14]. Hence, the presence of acetates and acetic acid in concentrated CO₂ solutions leads to an increase in the corrosion rate at near-neutral pH values compared to low pH values [15]. This is due to the decreasing pH of the solution by the HAc. With an increase in HAc concentration,

the corrosion rate showed a decreasing tendency, which might be due to the adsorption of HAc on the steel surface. However, studies conducted by Talukdar et al. [16] reported that in a CO₂-H₂S solution, the presence of lower concentrations of HAc increases the corrosion rate of carbon steel. In comparison, higher concentrations of HAc decrease the corrosion rate, but pitting corrosion is observed. [16,17]. This is due to the presence of high concentrations of hydrogen ions, which reduce the adsorption of H₂S on carbon steel, resulting in a lower anodic dissolution rate [15, 16, 17]. Thiosulfates exhibit inhibitive characteristics against CO₂ corrosion of mild steel, and their inhibition effect is related to the formation of iron sulfide on the steel surface [18].

This work aims to enhance the performance of 2-Acetylfuran (D) as a corrosion inhibitor at near-neutral pH (5.5) by adding different concentrations of sodium thiosulfate (H). Linear polarization measurements, potential and polarization curve techniques were used to investigate the behavior of the 2-Acetylfuran (D) on protection of mild steel samples immersed in 3.5% NaCl solution saturated with CO₂ gas.

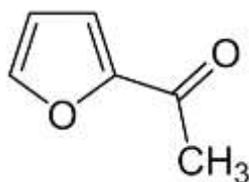
2. EXPERIMENTAL PROCEDURE

2.1 General

A 3.5% NaCl solution saturated with CO₂ gas was prepared by dissolving 35 grams of NaCl powder in one liter of deionized water for three hours before commencing the corrosion performance tests. The prepared solution had a pH range of 3.8 to 4. An amount of 8 mL of 1 molar sodium bicarbonate was added to the solution to adjust the pH to 5.5 when needed. The bicarbonate solution was prepared by dissolving 84 g NaHCO₃ in one liter of deionized water.

2.2 Inhibitor Solution

When Different concentrations (1, 2, 3, and 5 ppm) of 2-Acetylfuran (D) were used, the addition of 1 ppm of sodium thiosulfate pentahydrate, Na₂SO₃·5H₂O (H) (to study the effect on the potential and corrosion rate).



2.3 Mild Steel Working Electrode

Working electrodes made of commercial 1018 mild steel with a 0.785 cm² exposed surface area were used. Each sample was polished with emery paper up to 800 grit, rinsed with deionized water, and degreased using acetone. The time gap between polishing the specimens and immersing them in the corrosion cell was kept as short as possible and did not exceed 15 minutes, even in the worst cases.

2.4 Reference and Auxiliary Electrodes

Saturated calomel and platinum electrodes were used in this work.

2.5 Electrochemical Corrosion Cell

A standard Pyrex-type cell with a 1-liter volume made of glass. The lid has four inlets: one for the CO₂ bubbler, one for the electrode holder, one for the gas outlet, and one for injecting inhibitors. The cell was isolated from the air using a

rubber gasket. To ensure that the solution was saturated with CO₂ and the dissolved oxygen was removed, the CO₂ gas, free of oxygen, was bubbled into the cell for at least three hours. The saturated solution had a dissolved oxygen content of 5–15 ppb and a pH value of 3.8 to 4.

2.6 Electrochemical Equipment

An electrochemical measurement unit ACM - instruments, of twelve channels, controlled by a personal computer with the controlling and recording software, was used as the primary source for the data collection and enabled more repeatability of the tests. Linear Polarisation Resistance (L.P.R) or Rp and potential concerning calomel electrode were measured using the twelve-channel ACM equipment. The Rp measurements were carried out by polarizing the working electrode from –10 mV to +10 mV relative to the open-circuit potential, with a rate of 0.1 mV/s to minimize the effect of double-layer capacitance at the working electrode surface. The potential was measured with time for all tests to monitor the impact of the inhibitor on potential, which indicates the natural passivation by the inhibitor. All L.P.R and potential measurements were run for 20 hours. For greater accuracy, the performance of the inhibitor was checked at least twice to ensure consistent behaviour. The corrosion rate in mm/y of the samples was calculated using the following Stern-Geary equation

$$i_{cor} = \frac{\beta}{Rp}$$

Where

Rp is a corrosion polarization resistance in ohm.cm², and β is equal to 25 mV according to Stern Geary approach. The mild steel samples in the cell corrosion rate was calculated as follows:

$$CPR = \frac{i_{cor} M \omega}{n F \rho}$$

Where

CPR; Corrosion penetration rate (mm/y), Mw ;Molecular weight of mild steel 55.85 gm/mol, n; Number of electrons = 2, F; Faraday's constant 96500 c/mole and ρ; iron density = 7.87 gm/cm³

Hence

$$CPR \text{ (mm/y)} = \frac{301.6}{Rp}$$

Potentiodynamic polarization curves of cathodic and anodic polarization measurements were carried out for each sample immediately after L.P.R measurements. Polarization measurements were carried out by sweeping the potential from the open circuit potential to –500 mv to +500 mV with sweep rate of 1 mV/sec. The polarization curves were obtained by plotting the potential measured vs logarithm of current density.

3. RESULTS AND DISCUSSION

The results of polarisation resistance measurements and corrosion rate with time of mild steel in CO₂-saturated solutions at pH levels of 5.5 and 3.8, and stagnant conditions, are presented in Figs. 1 and 2. The objective of this experiment is to compare, in terms of corrosion rate, the performance of 5 ppm of inhibitor D at two different pH values in long-term tests. As shown in Fig. 1, the LPR values of the solution with a pH of 3.8 after the addition of 5 ppm of D give higher performance compared to those in the solution with a pH of 5, which is a less aggressive solution compared to the solution with a pH of 3.8. The decrease in polarization resistance indicates a reduction in the corrosion resistance of the system, as shown in Fig.2. Mild steel in the blank solution of pH 3.8 shows lower Rp resistance than that of pH 5.5

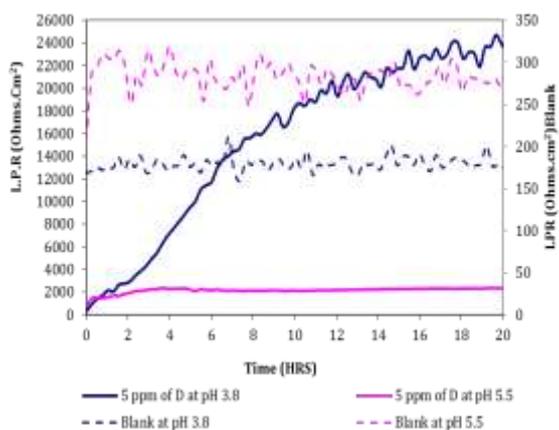


Figure 1. L.P.R values of mild steel immersed in 3% NaCl solution saturated with CO₂

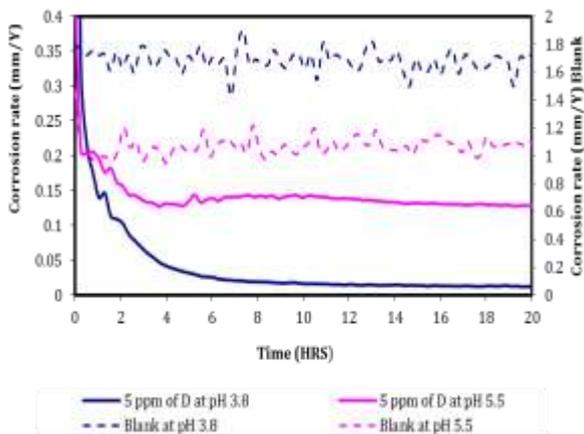


Figure 2. Corrosion rate of mild steel immersed in 3% NaCl solution saturated with CO₂

Figure 3 shows the comparison of polarization curves between blank samples at pH 5.5 and pH 3.8 and the effect of the addition of 5 ppm of D to both solutions. The results revealed that for the blank solutions, the current density was lower at pH 5.5 compared to that at pH 3.8; also, the potential of the mild steel at pH 5.5 was more negative than that at pH 3.8 (-741 mV and -618 mV, respectively). The addition of 5 ppm of inhibitor D to a 3.8 pH solution resulted in a decrease in potential, and the current density was significantly lower. In comparison, the addition of 5 ppm of inhibitor D to a 5.5 pH solution led to an

increase in the potential value and a slight decrease in the current density value.

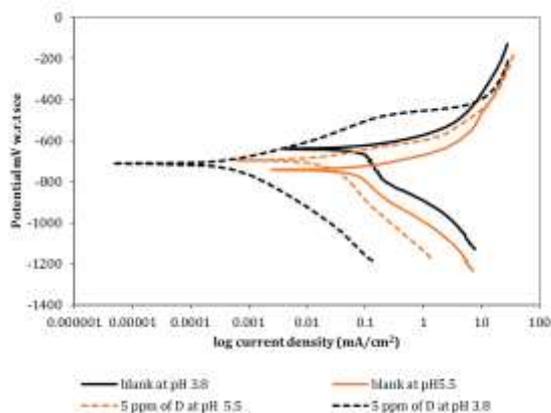


Figure 3. Potentiodynamic measurement carbon steel immersed in 3% NaCl solution saturated with CO₂

As the metal corrodes the corrosion potential increases. Figure (4) shows the behaviour of mild steel during the test at a pH of 5.5. The results in this figure reveal that the addition of 1 and 2 ppm of inhibitor D decreases the open-circuit potential compared to the blank sample (757, -789, and -731 mV, respectively, concerning SCE). The addition of 3 ppm and 5 ppm of D increases the potential towards a more positive value (-728 and -671 mV).

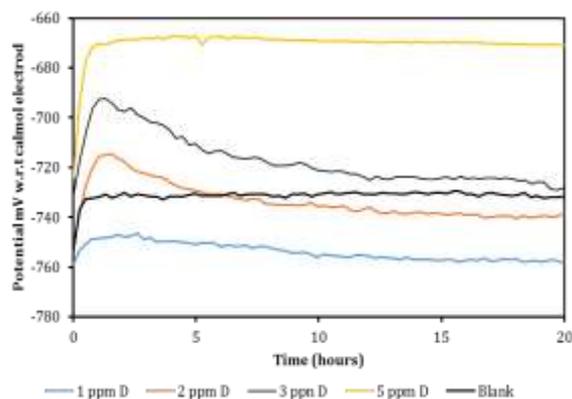


Figure 4. Potential w.r.t SCE at pH 5.5

Fig. 5 shows the effect of increasing the dosage rate when the inhibitor D is added to a 3.5% NaCl solution saturated with CO₂ at a pH value of 5.5, ranging from 1 ppm to 5 ppm. This figure also revealed that the addition of the chemical D decreases the corrosion rate of mild steel from 0.241 mm/y with 1 ppm of inhibitor D to 0.0821 and 0.071 mm/y with the addition of 2 and 3 ppm of inhibitor D, respectively. The corrosion rate increases to 0.128 mm/y with the addition of 5 ppm of inhibitor D, compared to 0.894 mm/y of the blank sample. The performance of the addition of 5 ppm of inhibitor D shows that the corrosion rate was found to be the lowest value of 0.142 mm/y after 8 hours of the test. The corrosion rate then increased to 0.128 mm/y at the end of the test, after 20 hours.

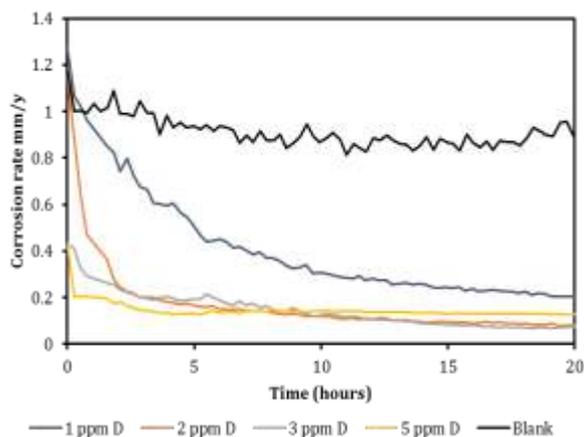


Figure 5. Corrosion rate of mild steel immersed in 3% NaCl solution saturated with CO₂ (mm/y) at pH 5.5

The following table shows the percentage of protection provided with the addition of different dosage of inhibitor D. The results in Table 1. Clearly showed that the maximum corrosion protection was obtained 92% with the addition of 3 ppm of the inhibitor D. Polarization measurements conducted after the end of the Linear Polarization Measurements (open-circuit potential (OCP) value becomes stabilized after 20 hours).

Table 1. Percent of corrosion protection of mild steel immersed in 3% NaCl solution saturated with CO₂ at pH of 5.5.

Dosage rate of Inhibitor (D) in ppm	% Corrosion Protection
1	73
2	81
3	92
5	86

The results of polarization curve of mild steel immersed in 3.5 NaCl solution saturated with CO₂ for three hours are presented in Fig. 6. The results showed that the addition of one, two, three and five ppm of inhibitor D shifted the corrosion potentials to more positive values. The values of the current densities of the mild steel treated with one, two and three ppm of D inhibitor are decreased, while the addition of five ppm of D leads to a significant increase in the current density, as shown in the figure. The figure reveals that the cathodic and anodic current density significantly decreases with the addition of 1 ppm, 2 ppm and 3 ppm of inhibitor D. The different behavior of cathodic current density with the addition of five ppm of D to the solution is observed. It indicates that the addition of increasing concentration of the D affects the cathodic reaction in the solution.

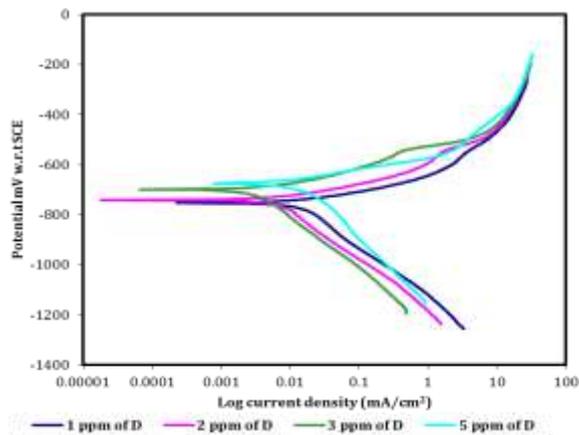


Figure 6. Potentiodynamic polarization curve of mild steel immersed in 3% NaCl solution saturated with CO₂ at pH 5.5

As the metal corrodes, the corrosion potential increases. Figure 7 shows the behaviour of mild steel during the test at pH 5.5. The figure shows that the addition of 1, 2, and 3 ppm of sodium thiosulfate solution increases the open-circuit potential compared to 3 ppm of inhibitor D (-696 mV, -676 mV, -651 mV, and -730 mV), respectively. The addition of 5 ppm of H, together with 3 ppm of D, results in a decrease in the potential again, towards a more negative potential value of -668 mV relative to SCE. Fig. 8 shows the effect of adding 1, 2, 3, and 5 ppm of sodium thiosulfate to 3 ppm of inhibitor D on the corrosion rate of mild steel in a pH 5.5 solution saturated with CO₂ gas. The figure shows that the addition of 1, 2, and 3 ppm of sodium thiosulfate (H) to 3 ppm of inhibitor D leads to a decrease in the corrosion rate from (0.011, 0.007 and 0.003 mm/y), respectively. The corrosion rate slightly increased to 0.004 mm/y with the addition of 5 ppm thiosulfate to 3 ppm of inhibitor D, compared to 0.069 mm/y with the use of 3 ppm of inhibitor D without the addition of sodium thiosulfate (H). Fig. 8 shows the effect of adding 1, 2, 3, and 5 ppm of sodium thiosulfate to 3 ppm of inhibitor D on the corrosion rate of mild steel in a pH 5.5 solution saturated with CO₂ gas. The figure shows that the addition of 1, 2, and 3 ppm of sodium thiosulfate (H) to 3 ppm of inhibitor D leads to a decrease in the corrosion rate from (0.011, 0.007 and 0.003 mm/y), respectively. The corrosion rate slightly increased to 0.004 mm/y with the addition of 5 ppm thiosulfate to 3 ppm of inhibitor D, compared to 0.069 mm/y with the use of 3 ppm of inhibitor D without the addition of sodium thiosulfate (H).

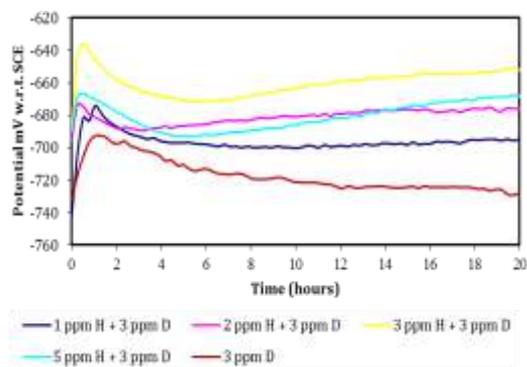


Figure 7. Potential measurement of mild steel immersed in 3% NaCl solution saturated with CO₂ at pH 5.5

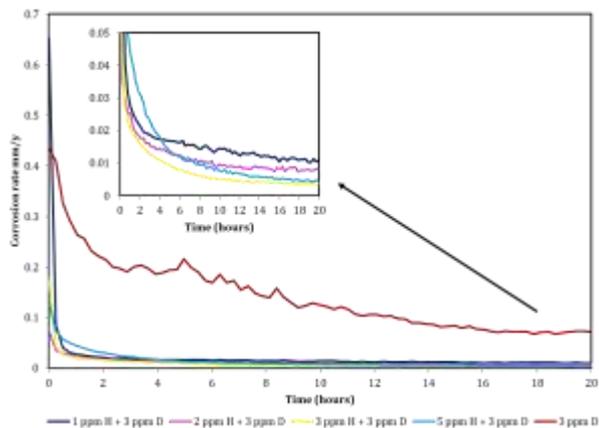


Figure 8. Corrosion rate of mild steel immersed in 3% NaCl solution saturated with CO₂ at pH 5.5

The enhancement of percentage of protection of mild steel from 91 % with addition of 3 ppm of inhibitor D and reached the maximum value of 99.7 with the further addition of 3 ppm of thiosulfate.

Table 2. Shows the percentage of protection gained by the addition thiosulfate to D inhibitor

Dosage rate ppm	3 ppm D	1 ppm H + 3 ppm D	2 ppm H + 3 ppm D	3 ppm H + 3 ppm D	5 ppm H + 3 ppm D
Percent Corrosion Protection	91	98.7	99.2	99.7	99.5

Polarization measurements are conducted after the end of the Linear Polarization Measurements (open-circuit potential (OCP) value becomes stabilized after 20 Hours). Polarization measurements were carried out at 1 ppm of H added to 3 ppm of D, 2 ppm of H added to 3 ppm of D, 3 ppm of H added to 3 ppm of D and 3 ppm of D. Fig. 9 shows the results obtained from the test. The results shown in figure revealed that the E_{corr} value of 1 ppm of H added to 3 ppm of D and 2 ppm H added to 3 ppm D moved to more negative values (-723.6 mV and -702 mV, respectively) compared to 3 ppm of D (-699.9 mV). Then it increases to the positive side (-695.6 mV) potential with an increase H concentration to 3 ppm compared to 3 ppm of D (-699.9 mV). On the contrary, the I_{corr} values decreases with increase in H concentration reference to 3 ppm of D. Another interesting feature is that the cathodic and anodic current density significantly decreases with the addition of 1 ppm, 2 ppm and 3 ppm of H with comparison to that of cathodic current density of 3 ppm of D. The value of cathodic current value of 1 ppm, 2 ppm and 3 ppm of H added to 3 ppm of D is approximately the same.

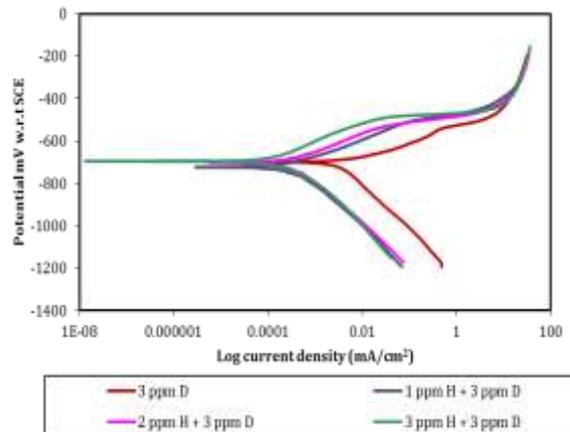


Figure 9. Potentiodynamic polarization curve of mild steel immersed in 3% NaCl solution saturated with CO₂ at pH 5.5

4. Conclusion

- High concentration of 2-Acetylfuran leads to a decrease in corrosion protection of mild steel at pH 5.5.
- Highest protection (99.7%) of mild steel at pH 5.5 was obtained by using 3 ppm of 2-Acetylfuran (D).
- Improvement of mild steel percent corrosion protection was observed by the addition of sodium thiosulfate (H).
- Addition of 5 ppm of sodium thiosulphate to 3 ppm of 2-Acetylfuran reduces the percentage of corrosion inhibition of mild steel.
- The highest corrosion protection of mild steel was obtained with a mixture of 3 ppm of sodium thiosulfate and 3 ppm of 2-Acetylfuran.
- The addition of sodium thiosulfate to 2-Acetylfuran significantly affects the cathodic current density of the mild steel and corrosion potential of the mild steel samples.

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