

Microbial corrosion inhibition of mild steel in salty water environment

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ABSTRACT

The use of antimicrobial corrosion inhibitor is increasingly being curtailed by recent corrosion restrictions. This paper represents the results of the study of new biocide, antimicrobial corrosion inhibitor named 8-hydroxy-*N'*-(2-(quinolin-8-yloxy)acetyl)quinoline-5-sulfonohydrazide (HQS) was used to inhibit corrosion causing sulphate reducing bacteria (SRB). The effects of the inhibitor on mild steel dissolution in salty water environment were studied through weight loss measurements, electrochemical and microorganism tests. The results obtained from this study show that, the new inhibitor can decrease corrosion and microbial growth under the conditions tested. The mass loss for the protected mild steel coupons shows lower corrosion rate compared to the unprotected one. Cyclic polarization test reveals that, the biocide minimizes the pitting area (hysteresis). The nature of protective film formed on mild steel was studied by scanning electron microscopy (SEM). SEM images revealed that, the corrosion inhibition by the HQS on the mild steel surface significantly improved in the presence of biocide.

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1. Introduction

Microbiologically influenced corrosion (MIC) has been defined as an electrochemical process in which the participation of microorganisms is able to initiate, facilitate, or accelerate the corrosion reaction without changing its electrochemical nature [1].

Bacteria corrode metals [2] and sulfate reducing bacteria (SRB) are responsible for the corrosion of cast iron, carbon steel, and low alloy steels, stainless steels, high nickel alloys and copper alloys. MIC mostly occurs under stagnant conditions or in operations with low or intermittent flow of river or sea water [3] and is problematic for the nuclear power plant, paper-making and oil industries [3,4]. MIC can cause considerable damage to cooling water systems [2], sewage treatment facilities [5], underground pipes and ships at low tide [4]. Black FeS films on stainless steel or mild steel are generally indicative of SRB attack, and when they are lifted, pits are revealed [4].

Bacteria in biofilms dominate most ecosystems [6,7]. To combat the problems caused by some biofilms, biocide treatment is widely used [8,9] to decrease biofouling and MIC in steel pipes [9] and in closed systems [8] but results are frequently unsatisfactory [10] since slowly growing bacteria within biofilms are much less sensitive to antibiotic activity [6,7].

However, the use of biocides is very expensive for industry [11,12] also can cause environmental pollution [11], and if they are used at concentrations in excess of a few ppm, they can be corrosive to metals [9]. Biocides are not as effective against sessile organisms within biofilms as against a planktonic population [10].

In this paper we used the antimicrobial 8-hydroxy-*N'*-(2-(quinolin-8-yloxy)acetyl)quinoline-5-sulfonohydrazide (HQS) to protect mild steel from corrosive attack by SRB. An electrochemical polarization (cyclic) was used to characterize the corrosion process. The corrosion rate was determined by using the weight loss method. In addition, scanning electron microscopy (SEM), was used to examine the electrode surface after the corrosion measurements.

2. Experimental

2.1. Materials

Working electrodes of mild steel electrode were used. The mild steel electrode was rectangular shape sealed in epoxy with an exposed area of 2 cm². The electrodes were polished with fresh emery paper different grades till fine mirror surface, washed with acetone before immersion. The counter electrode was a platinum (Pt) wire. A saturated calomel electrode was used as a reference electrode.

A two-compartment glass cell holding 250 ml solution was used in the test involving mild steel. Solutions were prepared from doubly distilled water and analytical grade chemicals. All measurements were conducted at 30 ± 2 °C. The potentiodynamic current–voltage characterization was recorded. The curves have been obtained by the computerized EG & G corrosion system. After attaining steady open circuit potential (O.C.P) the polarization was started from about 100 mV more negative than O.C.P to about 200 mV more positive than O.C.P, at a scan rate of 1 mV s^{−1}. After this forward half cycle, the scan was reversed to record the backward run.

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Biofilm bacteria (BF) included SRB and aerobic bacteria were developed from mild steel surface which immersed in Postgate medium B [13] inoculated with SMC-SRB for 7 days at 30 °C. A sterile safety razor can be used for collecting the BF. The succession enrichment and isolation of separate blank colony was done using Postgate medium B. to obtain SMC-SRB (stabilized mixed culture sulphate reducing bacteria).

2.1.1. Culture medium [13]

- (1) Postgate medium B, g l⁻¹ (ref) KH₂PO₄, 0.5; NH₄Cl, 1.0; CaSO₄, 1.0; MgSO₄·7H₂O, 2.0; sodium lactate, 3.5; yeast extract, 1.0; ascorbic acid, 0.1; thioglycolic acid, 0.1; FeSO₄·7H₂O, 0.5. The pH 7.5
- (2) Postgate medium E, g l⁻¹ (ref) KH₂PO₄, 0.5; NH₄Cl, 1.0; Na₂SO₄, 1.0; MgCl₂·6H₂O, 2.0; CaCl₂·H₂O, 1.0; sodium lactate, 3.5; yeast extract, 1.0; ascorbic acid, 0.1; thioglycolic acid, 0.1; FeSO₄·7H₂O, 0.5; agar, 15.0 (Postgate J. 1984).

2.2. Methods

2.2.1. Synthesis of

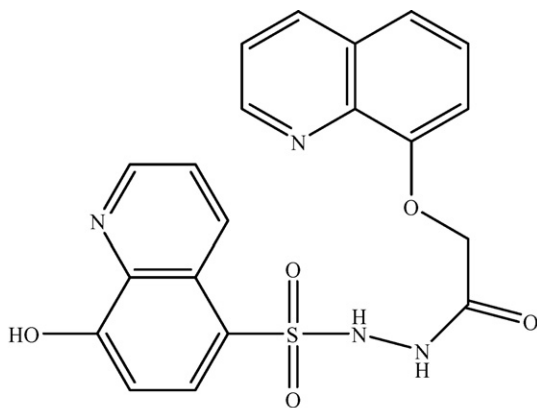
8-hydroxy-N'-(2-(quinolin-8-yloxy)acetyl)quinoline-5-sulfonohydrazide

2.2.1.1. Method A. 0.01 mol of 2-(quinolin-8-yloxy) acetohydrazide **2** was added to 30 ml of absolute ethanol, the mixture was stirred at room temperature till complete dissolution. 0.01 mol 8-hydroxyquinolin-5-sulfonyl chloride **3** was added to the mixture portion wise. The reaction mixture was heated under reflux for 6 h, then allowed to cool down to the room temperature. The formed solid was filtered off, air dried and crystallized from ethanol to afford 8-hydroxy-N'-(2-(quinolin-8-yloxy)-acetyl) quinoline-4-sulfonohydrazide, **1** as orange crystals (67%) mp: 260–263 °C.

2.2.1.2. Method B. 0.01 mol of ethyl 2-(quinolin-8-yloxy)acetate **4** was added to 30 ml of absolute ethanol, the mixture was stirred at room temperature till complete dissolution. 0.01 mol 8-hydroxyquinolin-5-sulfonylhydrazide **5** was added to the mixture. The reaction mixture was allowed to stir under reflux for 2 h. The formed solid was filtered off, dried and crystallized from ethanol to afford **1** (73%). C₂₀H₁₆N₄O₅S, M.wt 424.43.

2.3. Elemental analysis

Calculated %C, 56.60; %H, 3.80; %N, 13.20; Found %C 56.58, %H 3.80, %N 13.19; IR, ν 3949 cm⁻¹ (NH stretching), 1699 cm⁻¹ (C=O), 1429, 1195 cm⁻¹ (SO₂-N symm, asymm stretching); ¹H NMR (DMSO) δ 3.5–3.9 (broad, 2H, 2NH₂), δ 5.1 (2H, S), δ 7.0–9.5 (m, 11H, two quinoline ring protons), 10.6 ppm (S, 1H, OH group).



8-hydroxy-N'-(2-(quinolin-8-yloxy)acetyl)quinoline-5-sulfonohydrazide

2.4. Effect of (HQS) on the BF

The prepared coupons were washed and cleaned with acetone and alcohol and weighted before immersion in Postgate medium B contained the gradual concentrations from 50 to 600 ppm (HQS). 1 ml of enriched SMC-SRB was incubated in each bottle. All bottles were incubated at 30 °C for 3 months. After the incubation period finished sulfide concentrations were determined iodometrically [14] as a total sulfide for both sessile and planktonic SMC-SRB. The pH values were recorded before and after the incubation periods. The coupons were removed, cleaned and pickled in (1% HCl+0.5% thiourea) for 5–15 min according to thickness of BF. The planktonic bacteria related to the 35 ml which is the total volume used in experiment was detected. The sessile bacteria were determined related to (1 cm × 5 cm × 2 cm) which is the coupons area used in investigation. Coupons were removed from the bottles by the end of the incubation period, and the BFs scraped by sterile razor and collected in sterile bottles containing 30 ml Postgate medium B to be treated as plank-

tonic ones (incubation bottles treated to determine S⁻² and to detect minimum inhibitory concentration (mic) of (HQS) against sessile and planktonic bacteria. Corrosion rates were determined [15] from the weight loss for coupons before and after incubation period by the following formula:

$$CR = 534W/DAT$$

where CR = corrosion rate, mpy; W = weight loss, mg; D = density, g cm⁻³; A = area, in.²; T = time, days.

3. Results and discussion

3.1. Biocide activity

The effect of treatments on SRB activity was determined by measuring the concentrations of sulfide concentrations in the effluent (Fig. 1). The treatments were initiated when a high level of sulfide was measured in the effluent (average 117–189 mg l⁻¹). This corresponded with the formation of a thick black biofilm on the coupons which sulfide concentration (as SRB activity) dropped in the presence of biocide suggestion the suppression of SRB (Planktonic, Fig. 1, curve b) activity as a result of (HQS) treatments. Moreover, the inhibition of SRB activity has not been reported in sessile type (Fig. 1, curve a).

Fig. 2 shows the effect of concentration of biocide on the corrosion rate of mild steel in presence of SRB. As seen in Fig. 2 high corrosion rate are observed at first (absence of biocide—zero addition).

3.2. SEM investigation

The metal coupons exposed to solution free additive (biocide) had undergone several localized attack as can be seen from SEM investigation in Fig. 3(a). This can be attributed to simultaneous biofilm growth along with iron sulfide precipitation and biofilm formation due to the increased availability of nutrient species to the sessile SRB. Concentrations higher than 50 ppm till 600 ppm of (HQS) decreases significantly the corrosion rate to lower values as shown in Fig. 2. It was also noted that when the biocide concentration presented the optimum dose, SRB growth and corrosion rate were inhibited. This can be seen from SEM investigation (Fig. 3b) which shows the disappearance of localized attack and an improvement in the surface morphology of mild steel, if it's compared to

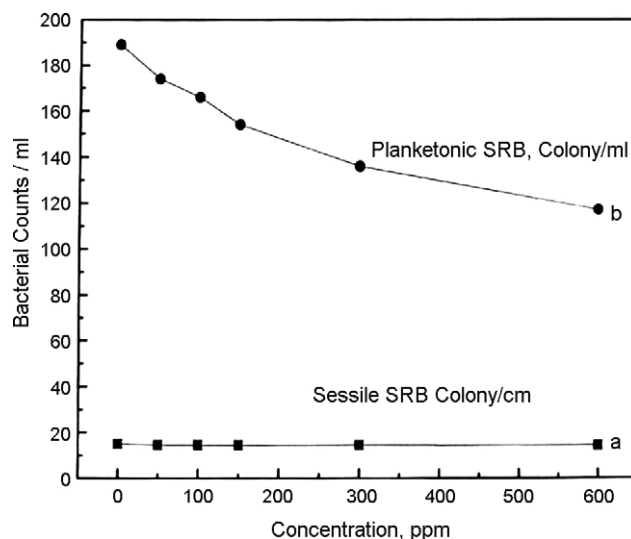


Fig. 1. Effect of concentration of HQS on sulfide activity of SM-SRB (Sessile-Planktonic).

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