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Bio-corrosion of carbon steel by sulfate reducing bacteria consortium in oil and gas pipelines

A. Abu Bakar[1], M. K. F. Mohd Ali[1], N. Md Noor*[1], N. Yahaya[1], M. Ismail[1] and A. Abdullah[2]

[1]Faculty of Civil Engineering, Universiti Teknologi Malaysia,
81310 , Skudai, Johor, Malaysia.
*Email : norhazilan@utm.my
Phone : +607-5538704
[2]Faculty of Chemical Engineering & Natural Resources,
Universiti Malaysia Pahang,
26300 Gambang, Pahang, Malaysia.

ABSTRACT

This research is aimed to give an overview of the impact of bio-corrosion on carbon steel grade API 5L X-70 immersed in growth medium and exposed to SRB consortium. Simulation of anaerobic corrosion conditions was carried out in a laboratory for 28 days. Raw crude oil gathered from the Baram Delta Operation Terminal was cultured in broth number 1249 (Modified Barr's Medium) to study the effect of bacteria growth upon metal loss. Carbon steel coupons grade X70 were cut to approximately 10mm x 20mm x 5mm and immersed in the cultured broth. During the experiment, the planktonic SRB were enumerated using a counting chamber (direct cell count method) under the electronic microscope at 200x magnification. Results indicated that the optimum pH and temperature for the respected SRB consortium genes were 8.5 and 37 °C, respectively. Metal loss of the corrosion specimen was measured and recorded after retrieval from the immersion period in the medium on a weekly basis prior to SRB inoculation for further analysis. The metal loss values supported that SRB activity can increase the metal loss of carbon steel against time of exposure. Additionally, the FESEM image showed the biofilm formations on the corrosion specimen. Thus, the results could conclude that bio-corrosion caused by particular local SRB consortium can be considered as a threat to carbon steel pipelines. Besides, the effect of SRB activity and response towards metallic materials in a dynamic environment is an interesting topic to be studied upon in the future.

Keywords: Sulfate-reducing bacteria; anaerobic corrosion; microbiologically influenced corrosion; bio-corrosion.

INTRODUCTION

Petroleum and gas are natural resources and are some of the major sources of energy globally. Pipelines have been used to facilitate shipments of crude oil and natural gas to consumers worldwide. For years, numerous failure reports of pipeline systems used to distribute crude oils throughout the country have been reported in local oil and gas operators. Failure investigation results have concluded that the pipes have most likely suffered severe corrosion damage due to Microbiology Influenced Corrosion (MIC). MIC is a process whereby the corrosion kinetic rate of a metallic material is accelerated by the

metabolic activity of microorganisms [1-3]. In the year 2000 at Carlsbad, New Mexico, a pipeline rupture accident involving MIC as the culprit cost twelve lives. A similar incident happened in the year 2005 where one of the four main import trunk lines into a storage tank onshore at the Baram Delta failed and failure investigations for both incidents indicated that MIC was a potential contributory factor [1, 2]. The Baram Delta fields are located in the South China Sea, specifically offshore of Sarawak and close to its boundary line with Brunei. It is between 20 and 45 km offshore and has been producing oil and gas since the late 1960s [4]. One of the MIC species known as Sulfate Reducing Bacteria (SRB) was found to be the largest colony present in the crude oil gathered from the Baram Delta. The role of SRB has been widely documented in relation to various corrosion reactions under anoxic/anaerobic conditions [6]. Hydrocarbons in petroleum may serve as electron donors for SRB, which use sulfate as the terminal electron acceptor for respiration resulting in sulfide production. The production of H_2S also causes the acidulation and plugging of petroleum reservoirs and the bio-corrosion of metal surfaces of pipelines and tanks [7]. Thus, recent research attention has been paid mostly to the development of a SRB-corrosion model with respect to its metabolic behaviour and the consequences for the bio-corrosion process.

This research was designed to explore the impact of bio-corrosion by local SRB consortium strains on carbon steel grade API 5LX70. The SRB consortium used in this study was cultivated from crude oil samples obtained from one of the main trunk lines of the Baram Delta Operation, Sarawak, Malaysia. The SRB's pH and temperature to proliferate were studied to ensure its optimal growth conditions during the experiment. A metal loss test was performed to observe the effect of SRB's bio-corrosion on carbon steel. Additionally, a Field Emission Scanning Electron Microscopy (FESEM) and an Energy Dispersive Spectroscopy (EDS) were conducted to observe the biofilm layer formed on the metal surface after exposure to the SRB.

METHODS AND MATERIALS

Microorganism Culturing and Growth Medium

The SRB consortium used in this study was cultivated from crude oil samples obtained from one of the main trunk lines of the Baram Delta Operation, Sarawak, Malaysia. The crude oil samples were collected and bottled at the Miri Crude Oil Terminal (MCOT). SRB kits (Sani Check, Biosan Lab. Inc., USA) were used to test its presence in the crude oil samples. A modified Baar's medium (Broth 1249) consisting of Magnesium sulfate at $7H_2O$ 4.096 g/L, Sodium citrate at $2H_2O$ 5.700 g/L, Calcium sulphate at 1.000 g/L, Ammonium chloride at 1.000 g/L, Potassium phosphate at 0.500 g/L, Sodium Lactate at 4.500 ml/L, Yeast at 1.000 g/L, and Ammonium iron (II) sulfate hexahydrate at 5.000 ml/L (this chemical composition should not undergo the autoclave process) was used as the selected medium of growth and cultivation of the SRB consortium. The standard pH of the medium was adjusted to 7.5 before being autoclaved at 121°C for 15-20 minutes. The medium was sparged using oxygen-free nitrogen after prior inoculation. SRB characteristics were detected in the selective growth medium. To ensure the presence of the SRB, the samples were then tested using the SRB kit (Sani Check, Biosan Lab. Inc., USA).

Materials

The corrosion specimens used in this study were machined from an actual pipeline segment of carbon steel grade API 5L X-70. Figure 1 shows the microstructure of the API

X-70 carbon steel under optical microscope and the chemical composition of the carbon steel is as follows; 97.093% Fe, 0.078% C, 1.67% Mn, 0.15% Ni, 0.012% P, 0.3% Si, 0.023% Cu, 0.275% Cr, 0.11% Ti, and 0.002% S [8]. The actual pipeline segment was cut into coupons with 10 mm x 20 mm x 5 mm dimension to fit into the anaerobic vial openings. The cleaned and dried coupons were then coated using prime coat, leaving only the top surface exposed. The surface was then polished with a grit Si-C paper grade 80,100, and 1000 into a mirror surface before being utilised in this experiment [9, 10].

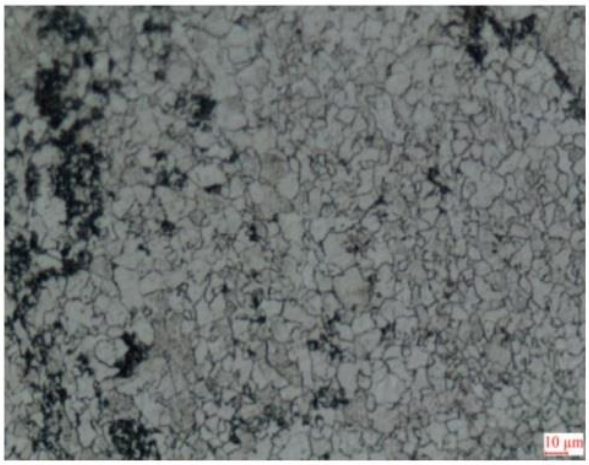

Figure 1. Microstructure of carbon steel API 5L X-70 under optical microscope.

Microorganism Enumeration Method

There are several bacteria enumeration methods. In this study, bacteria counting has been selected to enumerate the growth of bacteria; hence, a hemacytometer was used as the counting chamber. A cover slip was placed over the counting surface prior to adding the cell suspension after one drop of the medium sample had been put on it. The counting chamber was then placed on the microscope stage, and the counting grid was brought into focus at low power. One entire grid of standard hemocytometers with Neubauer rulings could be seen at 40x (4x objective).

Optimum pH and Temperature for Sulfate Reducing Bacteria Growth

One hundred ml of the Modified Baars media with different pH values was prepared in vials in an anaerobic condition, and 2ml of SRB seed was injected into the medium. The pH was adjusted by using a buffer chemical to 4.5, 5.5, 6.5, 7.5, 8.5, and 9.5, and the temperature was fixed at 37 °C. Precaution steps were taken to avoid contamination during the laboratory work. The vials were incubated for 28 days, and the growth of SRB was recorded using a spectrophotometer on selected days. The medium had turned into a black colour due to ferrous sulfide (FeS) [9] and produced the "rotten egg" smell [11]. This characteristic could be an indicator of the SRB's presence and their metabolism process [12].

Metal Loss Test

During the metal loss test, coupons were retrieved from the anaerobic vials every seven days (7th, 14th, 21st, and 28th days). The coupons were cleaned with a Clark's solution (a mixture of HCL and mineral solution) to remove all forms of dirt. The material used in this test was carbon steel coupon grade API 5L X-70. Samples were cut into 10mm x

20mm x 5mm dimensions to fit the anaerobic vial openings. The coupons were then dried and their weights before and after immersion in the medium were recorded and divided by the surface area of the coupon to determine the value of metal loss [13]. Values of weight loss and corrosion rate measurement were determined by applying the following equations;

$$Metal\ loss\ (W) = Wi - Wa \tag{1}$$

where Wi is the initial weight of coupon (g) and Wa is the final weight of coupon (g).

$$Corrosion\ Rate\ \left(CR, \frac{mm}{year}\right) = (K \times W)/(A \times T \times D) \tag{2}$$

where K is the constant (8.76×10^4), T is the time of exposure (yr), A is the surface area exposed (mm^2), W is the metal loss (g) and D is the density (g/cm^3).

FESEM Observation Test

The biofilms on the corrosion specimens were observed using FESEM (model Supra 35VP). Sessile microorganism was first fixed at 5% (wt) glutaraldehyde for 4 hours and then rinsed with a series of ethanol solution (25%, 50%, 75%, and 100% purities) to dehydrate the biofilm. Then, the specimens were dried using critical point dried (CPD) equipment with supercritical CO_2 and coated with gold (Au) prior to the examination of the biofilm under FESEM. The biofilm on the specimen surface was removed using Clarke's solution (ASTM G1-03) prior to the pits observation using FESEM.

RESULTS AND DISCUSSION

Optimum pH and Temperature for Sulfate-Reducing Bacteria Growth

An experiment to investigate the preferable environment for SRB growth based on pH (4.5, 5.5, 6.5, 7.5, 8.5, and 9.5) and temperature (37 °C) was performed in this research. The results showed that SRB will grow in the range of 4 to 9.5 pH according to certain genes. The growth pattern was observed based on the direct cell count of live SRB planktons. The counting process was done from an early period (day 3 and 5) of incubation, up to day 28 on a weekly basis. The presence of SRB was indicated by the formation of ferrous sulfide (FeS) as a reduction of sulfate (SO_4^{2-}) to sulfide (S^{2-}) which resulted in the black colour of the medium after day 2 or 3 of incubation. Figure 2 illustrates that from day 3 until day 14, the SRB had grown rapidly in mediums with pH 6.5, 7.5 and 8.5. However, slow growth rates were observed in highly acidic (pH 4.5 and 5.5) and highly alkaline (pH 9.5) medium conditions. Based on the cell counting, the highest number (cm/mL) of SRB growth was in pH 8.5 (alkaline condition) throughout the incubation of 28 days.

Throughout day 3 until day 14, the growth of sessile SRB kept increasing, but starting from day 21, the growth of sessile SRB had decreased until day 28. Every living microorganism needs a source of nutrients to proliferate. The decreasing growth of the planktonic SRB is due to the deficiency in the source of nutrients. According to Abu Bakar et. al, most of the SRB species thrive under optimum temperatures ranging from 30-38 °C [14]. This suggests that pH 8.5 is optimal for the SRB to proliferate and grow rapidly at 37˚C temperature. Furthermore, these microorganisms could alter the environmental conditions to suit their growth activity[10].

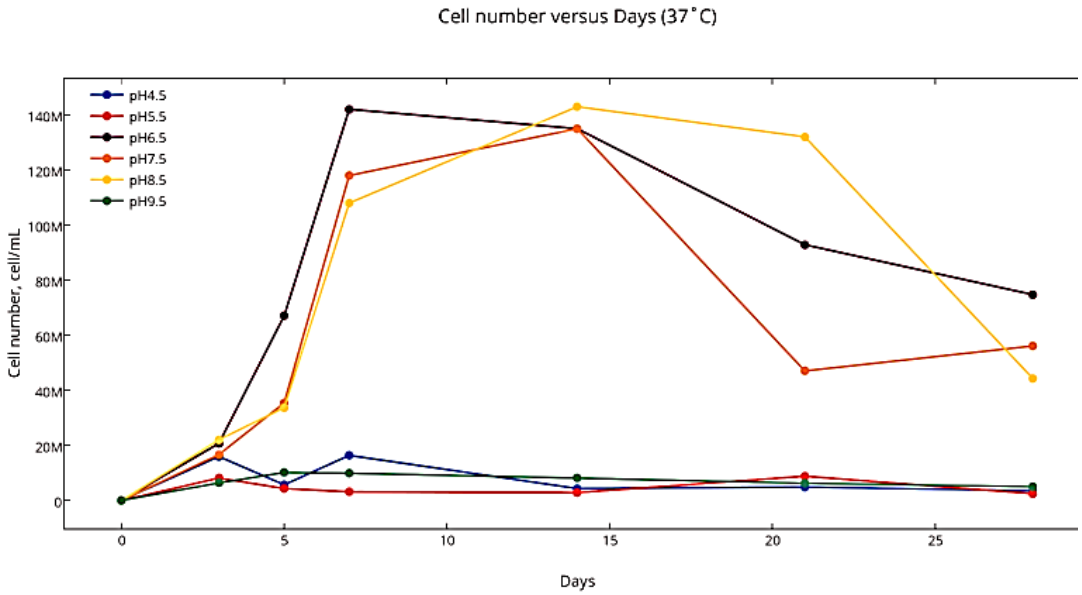

Figure 2. Effect of cell number against days at temperature 37 °C.

Weight Loss of Corrosion Specimen

Corrosion specimens used in the metal loss test were divided into two categories; specimens exposed to SRB activity (known as biotic), and specimens only exposed to the growth medium (known as abiotic). The corrosion specimens were left incubated in an incubator for 28 days at optimum pH 8.5 with temperature 37 °C and the samples were retrieved on a weekly basis (days 7, 14, 21, and 28). The corrosion specimens were cleaned and weighted using an analytical balance during the retrieval period. Figure 3 shows the cleaning process of the corrosion specimens using Clarke's solution before the weights of the specimens were taken. The cleaning process needs careful handling to avoid contamination which may affect weighing process [9]. After 28 days of immersion in the medium with SRB existence, biofilm and corrosion products were traced on the specimen's surface. The specimen's surface was scarcely visible since it was covered with a porous black layer.

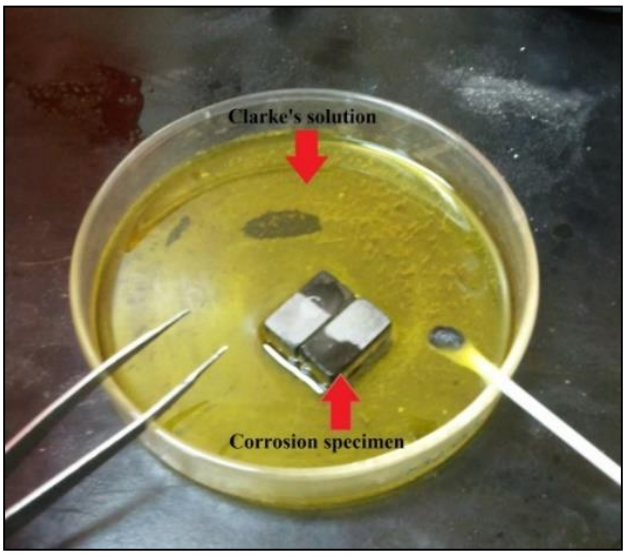

Figure 3. Cleaning of corrosion specimen using Clarke's solution.

Figure 4 illustrates the weight loss between biotic and abiotic samples at pH 8.5 and temperature 37 °C. From the graph of weight loss against time exposure, the result shows that the specimens exposed to SRB experienced a higher metal loss compared to the control sample from day 7 until day 28, while the weight loss for specimens in the abiotic sample increased directly against time exposure from day 7 until day 28. The findings revealed that the particular SRB gene used in this experiment could induce corrosion to occur and increase the weight loss of the specimens along with time exposure. This result is equivalent to a previous study by Abdullah et al. which stated that the sample consisting of a consortium of SRB had a higher corrosion rate compared to the sample without a consortium of SRB [15]. The pattern of the graph shows that the metal loss at day 14 was much lower compared to day 7's metal loss, but the metal loss started to increase again after day 14 until day 28. Furthermore, the corrosion rates calculated on day 28 of the biotic samples are more severe by a difference of 0.0183 mm/year compared to that of the abiotic samples which were 0.1453 mm/year and 0.1270 mm/year, respectively.

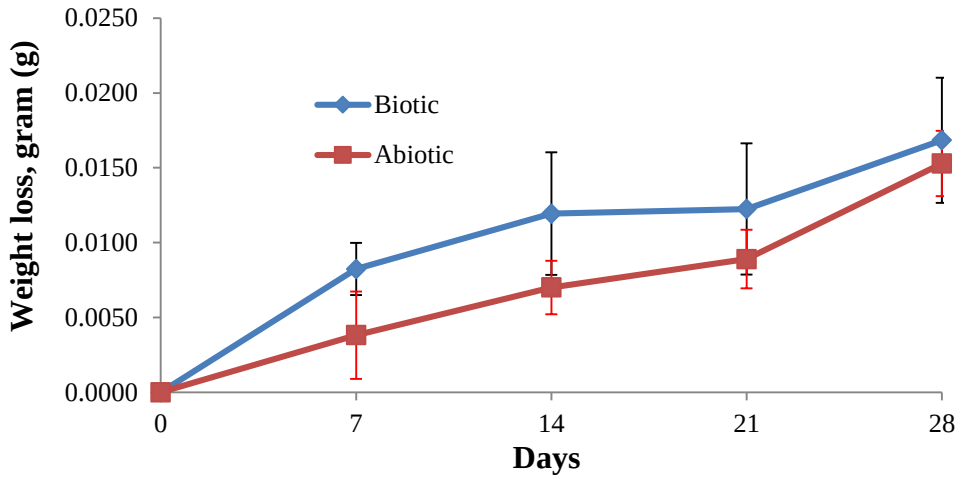

Figure 4. Variation of metal loss against time exposure (error bar: standard deviation, n = 6 for corrosion specimen)

Among the plausible explanations for these findings is the biofilm's development on the specimen surface. The biofilm was formed when the planktonic bacteria attached to the specimen surface became sessile bacteria. After the biofilm was developed, it may act as a corrosion inhibitor and perform as a passive layer on the surface of the specimen. As the biofilm established itself onto the specimen surface, it will create an anaerobic condition which is the most suitable environment for the SRB to grow secreting byproducts such as H_2S, and reacting with the specimen surface [16]. The SRB attached to the specimen surface will produce an Extracellular Polymer Substance (EPS). Based on previous research, the biofilm volume usually consists of 75-95% of corrosion products and EPS, while 5-25% of it is occupied by cells [17]. When the biofilm starts to develop, it starts to change the metal's electrochemical properties as well as physical properties [18, 19]. As for the SRB, the presence of ions such as sulfates and chloride which are found in the medium supports the formation of biotically-generated sulfides in the corrosion products [17]. Therefore, the longer the carbon steel is exposed to SRB, the more biofilm will be produced on the coupon's surface. This will cause an increase in the amount of metal loss and corrosion such as pitting that is dependent to time. Thus, the

formation of biofilm due to bio-corrosion will create severe corrosion effects in pipelines, tanks and other metals or alloys used in the industry. The species biochemical and physiological characteristics of the SRB are also factors affecting the bacteria's ability in the corrosion process [10].

FESEM Observation

Figure 5 (a) and (b) show the FESEM images of the biofilm with SRB genes on the carbon steel coupon surface and EDS analysis of the corrosion product, respectively. As illustrated in Figure 5(a), the planktonic SRB cells were observed to be in a rod shape at approximately 1.5-1.9 µm size. A higher weight loss value of specimen exposed to SRB was certainly due to the sulfide (S^{2-}) formation and SRB activity which produced hydrogen sulfide (H_2S) as a secondary metabolite [13]. Figure 5 (b) illustrates the EDS analysis of the corrosion products on the specimen surface which revealed a large amount of sulfur (S) and iron (Fe) peaks. Oxygen peaks were also revealed in the corrosion analysis due to oxygen exposure during the handling process. Fe^{2+} ions reacted with iron sulfide to form hydrogen sulfide due to the SRB's metabolism [20].

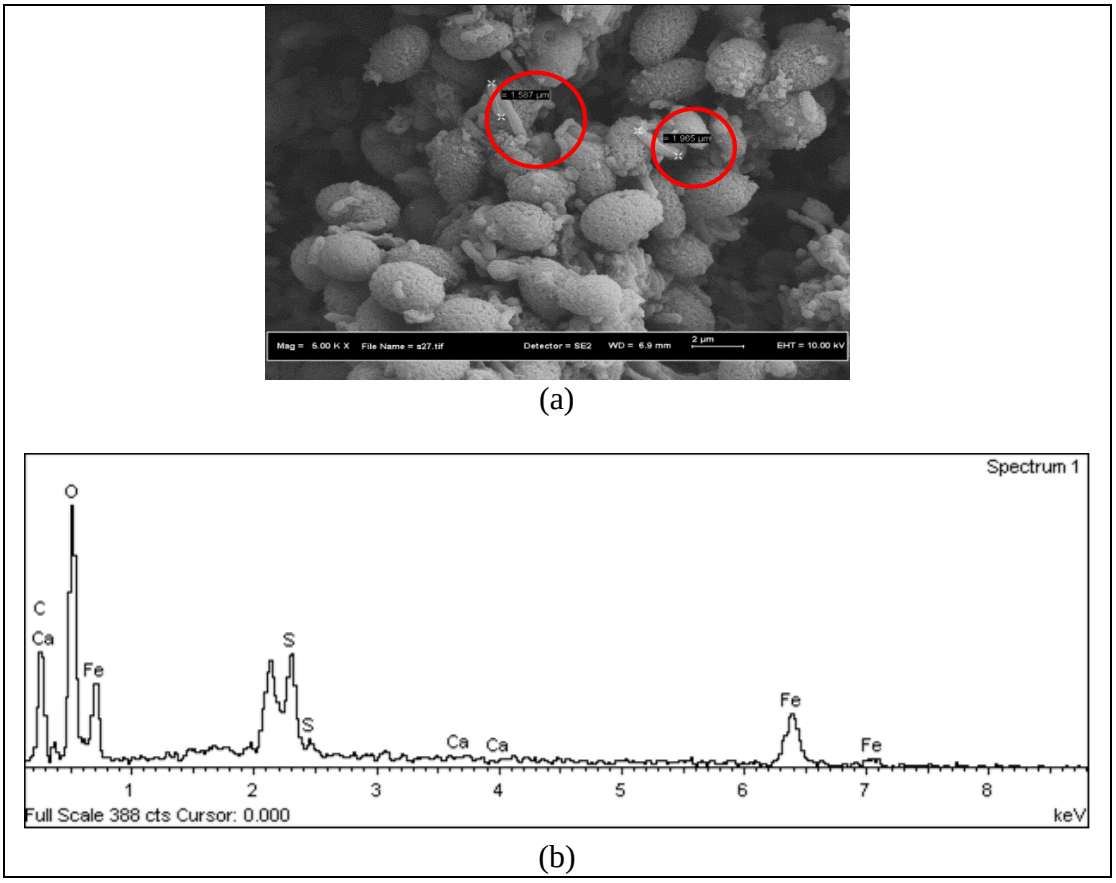

Figure 5. (a) FESEM image of the biofilm on the coupon surface for 21 days (rounded image shows the presence of SRB cells), (b) EDS analysis of corrosion product due to SRB metabolism.

CONCLUSIONS

This research was carried out to investigate the impact of SRB's existence from local sites on carbon steel grade API 5L X-70. Experimental results suggested that the optimum pH

and temperature of SRB consortium cultivated from the Baram Delta crude oil pipelines is 8.5 and 37 °C, respectively. The weight loss experiment showed that the weight loss of specimens exposed to SRB increased linearly (after day 7) over exposure to time. The FESEM observation and EDS analysis supported the finding of SRB's presence attached to the specimens' surface and showed high Fe and S peaks due to the presence of iron sulfide. The substantiation from this study suggested that the local SRB consortium can cause severe corrosion damage to the mentioned carbon steel grade. A number of important limitations need to be considered as the result of the weight loss, and the growth curve experiments in this research were performed in static conditions. Further research might explore the weight loss and growth of SRB in dynamic environments to investigate in more detail bio-corrosion behaviours under dynamic conditions. Nevertheless, in this study, no detailed genetic sequence was conducted to identify the type of SRB species present in the sample. However, it will be undertaken as future work for this research.

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