NCNE-2020 Special Issue

J. Indian Chem. Soc.,
Vol. 97, July 2020, pp. 1079-1082

Study of microbially influenced corrosion of mild steel in different media

S. Noyel Victoria* and Akansha Sharma

Department of Chemical Engineering, National Institute of Technology Raipur, Raipur-492 010, Chhattisgarh, India

E-mail: snvictoria.che@nitrr.ac.in

Manuscript received online 10 April 2020, accepted 12 June 2020

Mild steel is commonly used metal in many industries. The high concentration of iron in mild steel offers better strength making it preferred for many industrial applications. At the same time, mild steel is very susceptible to corrosion. Mild steel is the widely used material for ship ballast tank construction. Ship ballast tanks are helpful in maintaining the stability of the ships. The tank is usually filled with seawater. This causes corrosion of the ballast tank which could cause dangerous outcome. The corrosion of ship ballast tank by sulfate reducing bacteria is studied using weight loss studies. The medium used for the study is artificial seawater. The weight loss studies did not show a monotonic trend. The constantly varying weight loss values in both control and biotic media is due to the result of change in the thickness of corrosion products or biofilm layer. Maximum corrosion rate occurs in the first week of immersion which decreases in the second week and again increases little during the third week for all the media. The scanning electron microscopy images show significant growth of biofilms in the synthetic seawater medium with sulfate reducing bacteria (SRB).

Keywords: Mild steel, corrosion, seawater, SRB, lactate.

Introduction

Biocorrosion or microbially influenced corrosion of metals has become an unignorable issue at the industrial level[1]. Apart from industries, biocorrosion also affects the monuments, metal structures in the bridges built across the water bodies and fuel tanks in the aircrafts. The damages caused by biocorrosion are serious, because it causes not only loss to material and economy, but also loss of lives. Unlike corrosion caused by corrosive chemicals, the biocorrosion is difficult to control because of its complex nature[2].

Biocorrosion is generally the result of the activities of various microorganisms living in consortia. The microorganisms in the consortia may range from bacteria, fungi and algae. Though aerobic bacteria contribute to corrosion of materials, the role played by anaerobic bacteria is significant with the sulfate reducing bacteria (SRB) considered as the most corrosive[3]. Mild steel is the most extensively used metal in industrial environments particularly in refineries[4]. The biocorrosion is considered more complex because even with single bacterial community, the metabolism and activity depends on various factors such as temperature, duration of day light and availability of nutrients[5]. Apart from this, presence of one microorganism influences the growth and metabolism of other bacterial community either in a positive or negative way[5]. This manuscript is aimed at understanding the extent of biocorrosion of mild steel by *Desulfovibrio desulfuricans*, an SRB in different media using weight loss studies.

Experimental

Low carbon mild steel was used for the study. Mild steel coupons quantifying 10 mm by 10 mm were used as experimental specimens. The coupons were polished well to rule out any rough surface and washed well before the experiments. The coupons were immersed for different durations in growth medium prepared using synthetic sea water (medium-1) or nutrient broth with no lactate and less iron (medium-2). The composition of the medium-1 and medium-2 are provided in Table 1 and Table 2 respectively. Weight loss experiments using medium-1 were performed with and without bacterial culture (*Desulfovibrio desulfuricans*) in the medium. The samples that contained bacteria are referred to as biotic and those without bacterial culture have been mentioned as control. The corrosion studies using medium-2 were

Table 1. Composition of synthetic seawater growth medium

Chemicals	Concentration (g/L)	Chemicals	Concentration (g/L)
NaCl	24.53	Sodium citrate	5.0
$MgCl_2$	5.2	Calcium sulfate	1.0
Na_2SO_4	4.09	NH_4Cl	1.0
$CaCl_2$	1.16	K_2HPO_4	0.5
$NaHCO_3$	0.2	Sodium lactate 60%	3.5
KBr	0.1	Yeast extract	1.0
H_3BO_3	0.03	Ferrous ammonium sulfate	1.0
$MgSO_4.7H_2O$	2.0		

Table 2. Composition of the medium-2

Chemical	Concentration (g/L)
$MgSO_4.7H_2O$	0.1
K_2HPO_4	2.0
$CaCl_2$	0.1
Ammonium sulfate	0.1
Ferric chloride	0.02
Sodium thiosulfate	10.0

performed in the presence of SRB (biotic). Care was taken to ensure that the bacteria used for the corrosion studies are in stationary phase.

The weight of the specimen before and after immersion in the various media were measured and used for the corrosion rate calculation. The corrosion rate in mmpy is quantified using the formula:

$$CR = \frac{W \times 87.6 \times 10^4}{\rho A t} \quad (1)$$

The weight loss of the mild steel coupons after dipping in various media in g is denoted by W, ρ is the density of coupon in g cm^{-3}, A is the sample area in m^2 and t is the immersion time in h.

The morphology of the coupons immersed in medium-1 after one-week immersion was analyzed using SEM and the elemental composition of the deposits formed on the metal coupons was analyzed using EDAX.

Results and discussion

Weight loss results with medium-1:

The weight loss of the specimens immersed for different durations in medium-1 are provided in Table 3. The corresponding corrosion rates are also provided. The weight loss results for the first week show significant variation between the control and the biotic medium, whereas for further immersion periods, the difference between the weight loss of the mild steel coupons in control and the biotic media decreased. This difference is minimum for the sample immersed for three weeks. This could be due to the decrease in the number of active bacterial cells in the biotic media with immersion period.

Table 3. Weight loss results of mild steel coupons immersed in synthetic seawater medium at different immersion periods

	Biotic		Abiotic	
Duration (weeks)	Weight loss (mg)	CR (mmpy)	Weight loss (mg)	CR (mmpy)
1	30.76	2.05	20.55	1.37
2	22.4	0.75	16.2	0.54
3	35.6	0.8	33.2	0.74
4	27.5	0.46	21.6	0.36

The weight loss values and the corrosion rate in both control and biotic media decrease for second week and increase again for the third week and decrease further for the fourth week of immersion. This is owing to the formation of corrosion products layer in control and the biofilm layer in the biotic media. Studies show that the thickness of such layers tend to change with immersion time[6]. Beyond certain thickness the layer tends to detach form the metal surface which could be the happening during the second week and fourth week, thus facilitating the movement of corrosive medium towards the metal which increases the weight loss. The existence of thick layer on the metal surface poses diffusion resistance thus minimizing the corrosion. However, in the case of biotic media formation of biofilm is linked with the propagation of pitting corrosion[7].

Fig. 1 shows the SEM images of coupons submerged in medium-1 for one week. The sample in biotic media shows the presence of rod-shaped bacterial cells. The sample shows a continuous dark non-porous layer which could be due to the corrosion products and bright loosely packed layer which is non-continuous representing the biofilm. Table 4 gives the elemental composition of the mild steel coupons immersed in the control and the biotic media. The increased sulfur content is an indication of sulfide formation by the SRB. The

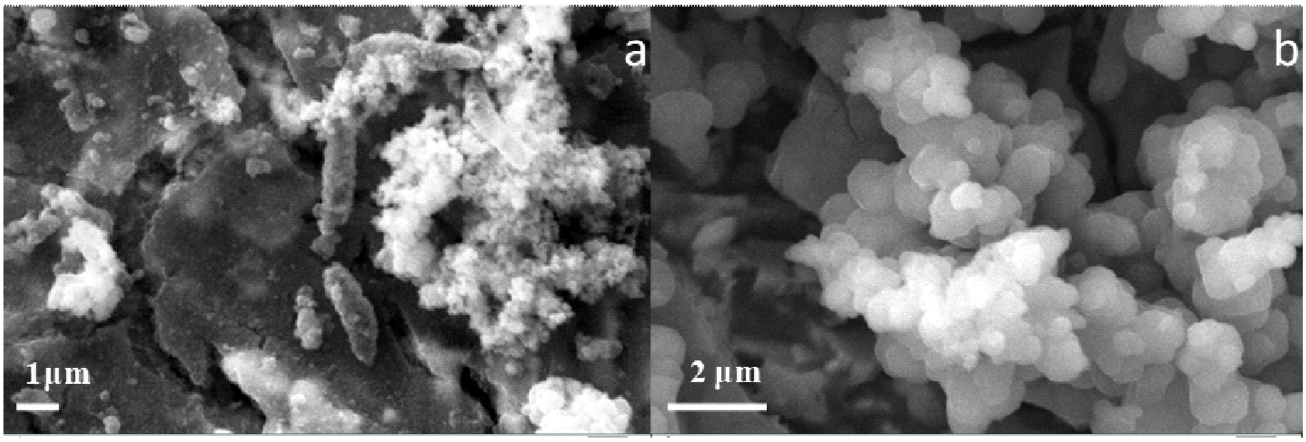

Fig. 1. SEM images of the mild steel coupons after one week immersion in synthetic sea water: (a) with bacteria and (b) without bacteria. Magnification used 20 kX.

Table 4. Elemental analysis of the mild steel coupons in synthetic seawater with SRB (biotic) and without SRB (control) at the end of first week of immersion

Element	Atomic (%)	
	Biotic	Control
O	41.79	24.96
C	28.65	38.14
Na	5.3	–
Mg	0.76	0.3
Si	0.23	0.37
P	0.95	–
S	0.55	0.46
Cl	6.08	–
K	0.1	–
Ca	1.07	–
Fe	14.55	35.28
Al	–	0.23
Mn	–	0. 26

presence of P, Ca, S indicate the presence of well grown biofilm[8]. The sample which was immersed in biotic medium showed higher concentration of oxygen which has been observed in many studies on *Desulfovibrio desulfuricans* biofilm and has been linked with corrosion[8]. The SEM images of the sample immersed in control show the presence of corrosion products layer.

Nutrient medium-2:

The weight loss values for the mild steel immersed in non-lactate and less iron containing medium (medium-2) are shown in Table 5. These results match well with the results reported by our group earlier with the medium-2 on mild steel with *Desulfovibrio desulfuricans*[9]. The corrosion rate and the weight loss values are lower for the mild steel coupons dipped in medium-2 when compared to the iron and lactate rich medium-1. The presence of lactate in iron rich medium has been reported to enhance the microbially influenced corrosion in the presence of SRB. This is because of the continuous utilization of the FeS formed by the reactions and preventing its deposition on the metal surface which would serve as a protection to minimize the corrosion[10].

Table 5. Weight loss results of mild steel coupons immersed in medium-2 with SRB (biotic) at immersion periods

Duration (weeks)	Biotic Weight loss (mg)	Biotic CR (mmpy)
1	2.3	0.153754579
2	1.9	0.063507326
3	4.4	0.098046398
4	4.2	0.070192308

There are various mechanisms proposed to explain the SRB induced corrosion in different kinds of environment. The medium-2 contains phosphate as the nutrient source and presents much lower corrosion values in the presence of SRB. It has been proposed that in the presence of phosphates, the below mentioned reactions are suggested to occur at the metal/liquid interface[11].

$$2KH_2PO_4 + Fe + 2OH^- \rightarrow Fe(H_2PO_4)_2 + 2KOH \quad (2)$$

$$KH_2PO_4 + Fe + 2OH^- \rightarrow Fe(HPO_4) + 2KOH \quad (3)$$

$$2Fe(HPO_4) + Fe + 2OH^- \rightarrow Fe_3(HPO_4)_2 + 2H_2O \quad (4)$$

Medium-2, consists of inorganic chemicals, and rich in phosphate which would result in the formation of phosphates of iron as suggested in earlier reports on inorganic medium as the nutrient source. The thickness of the biofilm and the concentration of phosphates in the biofilm were found to be high in such medium[11]. Similar studies using the medium-2, on mild steel corrosion in the presence of *Desulfovibrio desulfuricans*, by our group has shown increased phosphate content in the biofilm on elemental analysis[9]. Organic nutrient medium was found to be more corrosive and the thickness of the biofilm was less when compared to the biofilm of inorganic medium[11]. Consequently, the corrosion rate was also observed to be higher in organic medium. The thick biofilm and the insoluble phosphates were found to decrease the corrosion rate of the mild steel in inorganic medium[11].

Conclusions

The corrosion of mild steel influenced by *Desulfovibrio desulfuricans* depends strongly on the composition of the nutrient medium. The lactate in iron rich medium has been observed to enhance biocorrosion of mild steel. The mild steel immersed for one week in the SRB containing synthetic seawater shows the presence of mature biofilm. The corrosion rate and the weight loss values show non-monotonic trend due to the continuously changing biofilm thickness. The medium which contained phosphates showed lower corrosion rate when compared to the synthetic seawater medium.

Acknowledgements

The corresponding author would like to acknowledge National Institute of Technology, Raipur, India for funding the project through the Seed Grant Project NITRR/Seed Grant/ 2016-17/010.

References

1. C. A. Loto, *Int. J. Adv. Manuf. Technol.*, 2017, **92**, 4241.
2. F. Mansfeld, *Electrochim. Acta*, 2007, **52**, 7670.
3. H. Venzlaff, D. Enning, J. Srinivasan, K. J. J. Mayrhofer, A. W. Hassel, F. Widdel and M. Stratmann, *Corros. Sci.*, 2013, **66**, 88.
4. J. R. Becker, "Corrosion and Scale Handbook", 1st ed., Pennwell Publishers, 1998, Chap. 4, p. 57.
5. M. Eashwar and S. Maruthamuthu, *Biofouling*, 1995, **8**, 203.
6. B. S. Swaroop, S. N. Victoria and R. Manivannan, *J. Taiwan Inst. Chem. Eng.,* 2016, **64**, 269.
7. I. B. Beech and C. C. Gaylarde, *Rev. Microbiol.*, 1999, **30**, 177.
8. F. L. Heggendorn, A. G. M. Fraga, D. C. Ferreira, L. S. Goncalves, V. O. F. Lione and M. T. S. Lutterbach, *Int. J. Dent.*, 2018, **2018**, 1.
9. S. Chaithra, Apeksha gupta, R. Manivannan and S. Noyel Victoria, *Indian J. Chem. Tech.*, 2019, **25**, 441.
10. D. Enning and J. Garrelfs, *Appl. Environ. Microbiol.*, 2014, **80**, 1226.
11. A. Rajasekar and Y. P. Ting, *Indian Eng. Chem. Res.,* 2011, **50**, 12534.