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Biological corrosion inhibition of steel alloy by pani nano fiber

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Sulfate-reducing bacteria are recognized as a major group of microorganisms linked to anaerobic corrosion. Polyaniline is a good inhibitor for microbially influenced corrosion. The polyaniline nanofibres were prepared by interfacial polymerization method and the prepared polyaniline nanofibres were coated on steel coupons. These steel coupons were used for corrosion studies using sulphate reducing bacteria and compared with and without polyaniline nanofibre by weight loss measurements. 5th day polyaniline coated steel coupon inoculated with sulfate-reducing bacteria gave a low corrosion rate and high inhibition efficiency. The polyaniline nanofibre inhibits the corrosion level of the steel coupons induced by sulphate reducing bacteria.

Key words: Microbially influenced corrosion (MIC), sulfate reducing bacteria (SRB), polyaniline (PANI) nanofibre.

INTRODUCTION

Corrosion can be classified regarding the nature of the process. Physicochemical interactions between a metallic material and its environment can lead to corrosion. Electrochemical corrosion is a chemical reaction involving the transfer of electrons from zero violent metal to an external electron acceptor, causing release of the metal ions into the surrounding medium and deterioration of the metal (Beech, 2004; Javed et al., 2015). Usually corrosion is of an electrochemical nature, but there is also a chemical corrosion not involving charge transfer, like the corrosion of steel in liquid sodium. Presently, oil recovery and transportation are accompanied by serious problems connected with corrosion fracture of the equipment and pipelines of the oil and gas industry. The first signs of deterioration of pipelines were detected in the 1970s. However, the causes and mechanisms of stress corrosion of steel structures have not been determined exhaustively until the present despite the intense study of the problem (Dowling and Guezennec, 1997; Gangloff and Kelly, 1994; Videla, 1996a; Wilmott et al., 1996; Wilmott, 1997). In the first turn, this is connected with the complex nature of the stress corrosion process

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where numerous dissimilar factors interact. The main volumes of oil are extracted by the method of keeping the formation pressure with the use of highly mineralized formation waters. Oil-field brines contain a high amount of chloride ions, oxygen, carbon dioxide and hydrogen sulfide and stimulate the appearance and development of local electrochemical processes that produce the most dangerous corrosive and fracturing effects on the metal. In practical, oil recovery formation pressure is often kept with the help of surface waters of close-lying sources, which contain numerous microorganisms. Adapting themselves to the conditions of the formation, the micro-organisms produce sulfate-reducing bacteria (SRB). Precipitating on the surface of the metal SRB emits hydrogen sulfide and organic acids, for example, acetic acid, which is very aggressive with respect to carbon steel (Nizhegorodov et al., 2008). Biocorrosion is a result of interactions, which are often synergistic, between the metal surface, abiotic corrosion products and bacterial cells and their metabolites (Beech and Sunner, 2004). Bacterial adhesion and bio-film formation are commonly encountered both in natural environments and in industrial processes (Marshall et al., 1994). The heterogeneous bio-film and the associated bacteria form complex biological systems that can cause several chemical changes at the metal/bio-film interface, such as producing gradients in pH, dissolved oxygen, chloride and sulfate (Lewandowski, 1994; Boronstein, 1994). Under aerobic conditions, the microbial colonization usually leads to the formation of differential aeration and concentration cells due to the metabolism of the bacterial colony. The generation of these concentration cells is widely recognized to be detrimental to the integrity of the passive film and to facilitate the initiation of pitting or crevice corrosion (Little et al., 1992). The above process is well known as micro-biologically influenced corrosion (MIC) or a biocorrosion phenomenon. The use of coatings is the most common means of corrosion control for materials susceptible to environmental interactions. A coating may act as an ionic filter with sufficiently high electrical resistance to mitigate current transfer between anodic and cathodic sites when water permeates the coating. Coatings may also act as a barrier to oxygen diffusion to impede the cathodic reaction. Overall, the chief function of such coatings is to provide an effective environmental barrier to the substrate, thereby preventing corrosion (Shifler, 2005). However, much is unknown on the specifics of how organic coatings fail. There is a lack of understanding of the complex, multi-variable degradation processes leading to coatings failure. Water and oxygen can permeate, at least to some extent, through any amorphous polymer film, even when the film has no imperfections such as cracks or pores (Charaeklis, 1990). Polyaniline (PANI) ranks among electrically conducting polymers. Its high conductivity and chemical variability makes it suitable for a number of applications (Samui and Phadnis, 2005; Sathiyanarayanan et al., 2005). In the course of polymerization, PANI has the ability to create thin conducting films with very good adhesion on various base materials. So this polyaniline nanofibres was used as an corrosion inhibitor for the corrosion inhibition studies.

MATERIALS AND METHODS

Collection of samples

The corroded material was scraped from the metal rods placed in sterile container and was transferred to the laboratory for further use.

Isolation and cultivation of sulphate reducing bacteria

The sulphate reducing bacteria present in the collected corroded material was isolated and cultivated. One gram of the scrapped material was aseptically inoculated on 100 ml of sterile lyngby medium (peptone: 20.0 g/L, agar: 12.0 g/L, sodium chloride: 5.0 g/L, beef extract: 3.0 g/L, yeast extract: 3 g/L, L-cysteine: 0.6 g/L, ferric citrate: 0.3 g/L and sodium thiosulphate: 0.3 g/L). After inoculation, it was incubated at 37°C for 24 h, in a shaker incubator. A loopful of lyngby medium broth culture was inoculated in 100 ml of sterile postgate medium (Videla, 1996b) (pottasium dihyrogen phosphate: 0.5 g/L, ammonium chloride: 1.0 g/L, sodium sulphate: 4.5 g/L, calcium chloride: 0.6 g/L, magnesium sulphate: 0.6 g/L, sodium lactate: 6.0 g/L, yeast extract: 1.0 g/L, ferrous sulphate: 0.04 g/L and sodium citrate: 0.003 g/L). After inoculation, it was incubated at 37°C for 24 h, in a shaker incubator. A loopful of bacterial culture grown in Postgate medium was streaked on sterile postgate agar plates. It was incubated at 37°C for 24 h. After incubation, the plates were observed for morphologically different bacterial cultures.

Identification of the isolates

The bacterial isolates grown on postgate agar medium were identified based on the microscopic, morphological and biochemical characters (Holt et al., 1994).

Preparation of polyaniline (PANI) nanofibres

PANI nanofibre was synthesized by interfacial polymerization method as described by Huang and Kaner (2004). 5.6 g (60 mmol) of aniline was dissolved in 200 ml of chloroform and 3.4 g (15 mmol) of ammonium per sulphate was dissolved in 200 ml of 1.5 mol/L HCl solution. These two solutions were carefully transferred in a 1000 ml beaker, generating an interface between two layers. The reaction was carried out in an interface of the two phases at room temperature for 24 h. The protonated PANI nanofibres were obtained and then converted into emeraldine base form by treatment with 10% weight of aqueous ammonium solution for 24 h.

Preparation of steel coupon

Approximately 5.2 x 1.3 x0.5 cm steel coupons was obtained from local steel agencies and was used for the biocorrosion studies. To remove the impurities, the steel coupons were immersed in concentrated HCl for overnight and were washed with distilled water. The washed steel coupons were washed in acetone for 30 min and were dried in air. The cleaned steel coupons were sequentially ground with 180 and 500 grit emery papers to get

finally polished smooth surface steel coupons.

Preparation of PANI- polyvinyl acetate (PVA) coating

Polyvinyl acetate (PVA) was used as a base matrix for dispersing PANI (2.5% weight) over the steel coupons. 2.5% (weight) of the conducting polymer in the coating was sufficient for achieving good corrosion resistant (Cao et al., 1989). So, in the present study, the same procedure was used for the preparation. 2.5% of PANI was dispersed in 99% of chloroform. The suspension was vigorously agitated using shaker for 24 h. In another beaker, PVA (10 weight %) was dissolved in chloroform. The two solutions were mixed and stirred (4.5%) until a homogenous dispersion was formed. Film thickness can be controlled by varying the duration of the substrate dipping time (Avlyanov et al., 1995); the cleaned steel coupons were coated with the prepared PANI-PVA matrix by dipping for 1, 3 and 5 days. After coating, the coated steel coupons were placed in hot air oven at 65°C for 12 hfor curing process. After curing, the steel coupons were used for the biocorrosion studies.

Biocorrosion inhibition by PANI-PVA matrix

The biocorrosion inhibition level of PANI-PVA matrix was analyzed using sulphate reducing bacterial isolate. To compare the level of biocorrosion inhibition, the same numbers of coupons were exposed to the sterile nutrient rich medium which had exactly the same composition but the exception is without inoculating any microorganisms. All the experiments were carried out in a batch mode under stagnant condition in an incubator at 25°C. A loopful of 24 h SRB broth culture was aseptically inoculated on to 50 ml of the sterile postgate broth. After the OD value reached a level of 1.0, the steel coupons (with and without coating) were hung on the nylon string and were aseptically introduced into the 50 ml of grown broth cultures. To maintain the bacterial density, the steady-state growth phase throughout the experiment, a semi-continuous mode were employed, that is, 75% of the medium were drained and replaced with an equal amount of fresh medium for every 7 days. On days of 7, 14, 21, 28, 35 and 49, the coupons were retrieved from the inoculated medium for weight loss measurement and bacterial colonization studies with stereo trinocular microscope.

Analysis of corrosion

Measurement of weight loss (Umoren et al., 2007)

The steel coupons were immersed in 20% NaOH solution containing 200 mg zinc dust, scrubbed with bristle brush under running water in order to remove the corroded particles, dried and reweighed. The weight loss was taken as the difference between the weight at the given time and the initial weight of the test coupon was determined, using the digital balance. The measurement was carried out for the blank, with anti-corroding agent coating and without coating. The inhibition efficiency was evaluated using the equation:

$$I\ \% = (1-W_1/W_2) \times 100$$

Where W_1 and W_2 are the weight loses (mg) for mild steel in different time exposure both coated PANI nanofibres and uncoated coupons have been determined from the weight loss measurement using an expression. The corrosion rate was evaluated using the equation:

$$\text{Corrosion rate (mg cm}^{-2}\ \text{h}^{-1}) = \Delta w / AT$$

Where, Δw is the weight loss (mg) (obtained as a difference between initial weight and weight at a given time), A is the area of specimen (cm^2) and T is the exposure time (h).

Analysis of bacterial colonization in steel coupons using fluorescence microscope (Walker and Keevil, 1994)

At the predetermined period of bacterial incubation, the specimens were retrieved and washed twice with a sterile phosphate buffered saline (PBS) solution, to remove the dead and loosely attached bacteria. The fixation of bacterial cells with 2.5% glutaraldehyde PBS solution for 4 h, the specimens were washed twice with sterile phosphate buffered saline (PBS) solution and deionized water, followed by staining with 0.01% Acridine orange solution for 10 min. The excess dye was removed by washing with 70% alcohol solution. The specimens with immobilized bacterial cells were imaged under 1000x magnification using a stereo trinocular microscope.

RESULTS AND DISCUSSION

The beginning of the anaerobic period is associated with an increase of the corrosion rate attributed to micro-organisms; SRB (Enning et al., 2015). The corroded material was scrapped from the metal rod and used in the present study for the isolation of sulphate reducing bacteria. The SRB was isolated by inoculating the corroded material in lyngby medium. The grown cultures was further sub cultured on postgate medium and finally streak plated on postgate agar medium. The morpho-logically different colonies observed in postgate agar medium were used for the identification procedure. Cultural characters of the isolates grown on lyngby medium and postgate agar medium were observed. Based on the morphological, microscopical and biochemical characters of the isolates, they were identified as sulphate reducing *Desulphovibrio* sp. (Table 1 and Figure 1). Desulfovibrio profundus was one such SRB associated in carbon steel corrosion (Lanneluc et al., 2015).

Biocorrosion inhibition by PANI-PVA matrix

MIC of steel is a serious problem in the marine environ-ment and many industries, such as power generation, petrochemical, pulp and paper, with serious safety and economic concerns (Walsh et al., 1993). The use of coatings is the most common means of corrosion control for materials susceptible to environmental interactions. Electrically conducting polymers have been shown to be effective for corrosion prevention (Liu and Levon, 1999). The biocorrosion inhibition level of PANI-PVA matrix was analyzed using sulphate reducing *Desulphovibrio* sp. Yuan et al. (2012) also observed that PVAn-PANI bilayer coating is having good corrosion inhibition against SRB. The corrosion rate of uncoated sterile and SRB containing steel coupon were analyzed in various days (Table 2 and Figure 2) and the corrosion rate were

Table 1. Morphological and biochemical characters of the isolate.

Culture	Growth in lyngby broth			Growth in Postgate medium		
	Morphological characters of the isolate					
SRB	H_2S production (black color formation)			Small colonies		
	Biochemical characters of the isolate					
Gram staining	**Shape**	**Lactate utilization**	**Malate utilization**	**Pyruvate utilization**	**Actate utilization**	**Growth at NaCl**
Gram negative	Rod	positive	positive	positive	positive	No growth

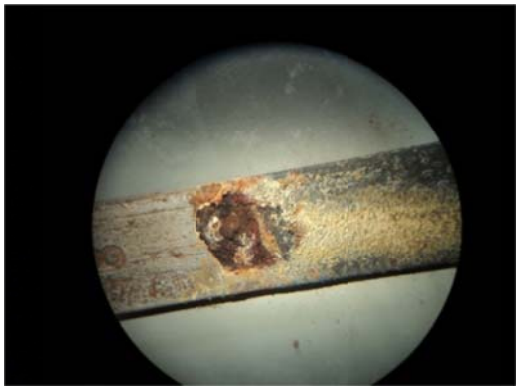

Figure 1. Stereo trinocular microscopical view of sulphate reducing *Desulphovibrio* sp.

Table 2. Comparison of corrosion rate in sterile medium and with SRB (without coating).

	Corrosion rate at different days (mg cm^{-2} h^{-1})						
	1st day	**7th day**	**14th day**	**21st day**	**28th day**	**35th day**	**42nd day**
Corrosion rate in sterile medium	-	-	0.0017	0.0035	0.0052	0.0056	0.0063
Corrosion rate in SRB containing medium.	0.010	0.0272	0.0348	0.0349	0.0391	0.0419	0.0422

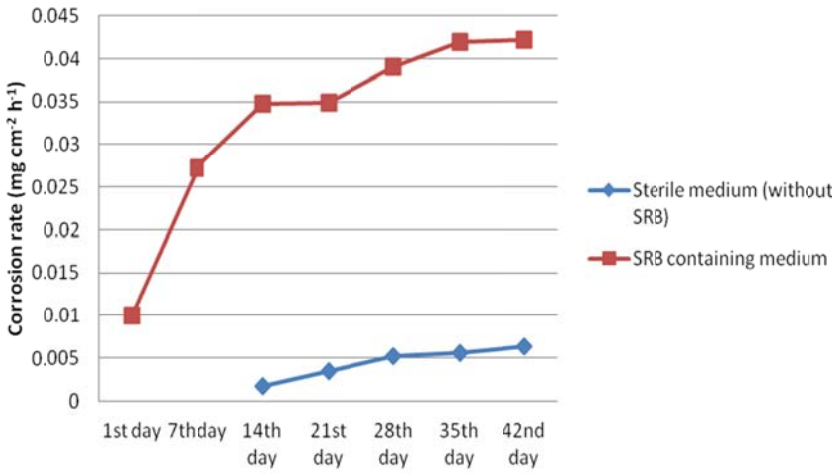

Figure 2. Comparison of corrosion rate in sterile medium and with SRB (without coating).

Table 3. Corrosion rate in SRB containing medium at different days with PANI nanofibre coating and without coating.

SRB containing medium	Corrosion rate at different days (mg cm^{-2} h^{-1})						
	1st day	7th day	14th day	21st day	28th day	35th day	42nd day
Uncoated coupons	0.010	0.0272	0.0348	0.0349	0.0391	0.0419	0.0422
1st day coated coupons	-	0.007	0.007	0.011	0.013	0.015	0.014
3rd day coated coupons	-	0.003	0.004	0.009	0.009	0.010	0.010
5th day coated coupons	-	-	0.004	0.009	0.009	0.009	0.01

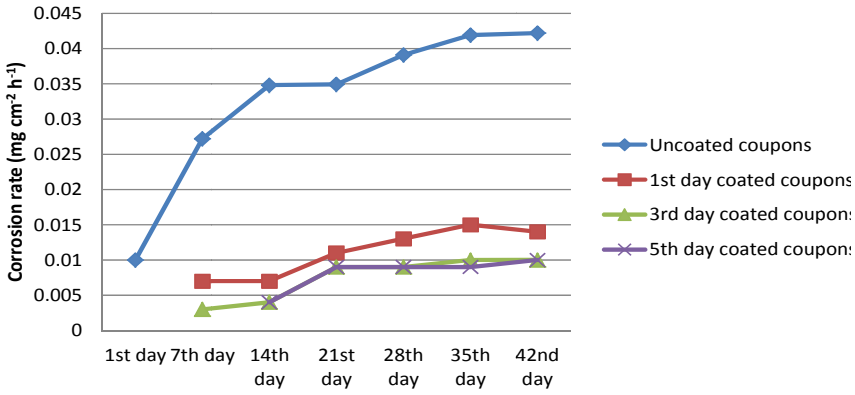

Figure 3. Corrosion rate in SRB containing medium at different days with PANI nanofibre coating and without coating.

Table 4. Inhibition efficiency for PANI nanofibres steel coupons for 1, 3 and 5 days.

	Inhibition efficiency at different days (%)						
	1st day	7th day	14th day	21st day	28th day	35th day	42nd day
Sterile medium	-	-	-	68.2	33.8	21.8	21.4
1st day	-	77.3	76	76.3	66.3	62.6	65.9
3rd day	-	88.2	88.1	79.6	76.0	75.6	74.3
5th day	-	-	88.5	80.2	76.8	75.2	70.9

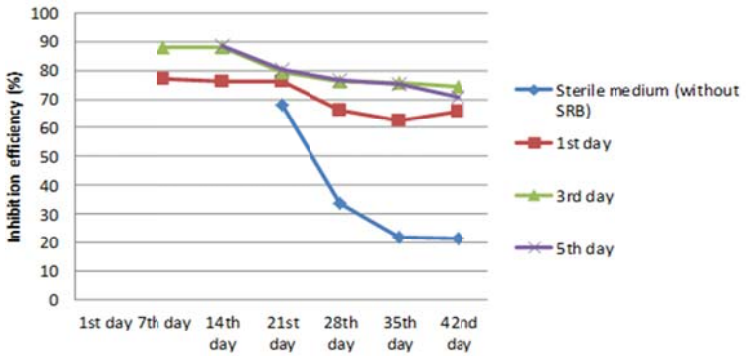

Figure 4. Inhibition efficiency for PANI nanofibres steel coupons for 1, 3 and 5 days.

increased, with time of the incubation period. With the corrosion rate in the presence or absence of SRB (Table 3 and Figure 3), there is increase in corrosion rate in the presence of SRB. When the same study with the coated PANI steel, there was increasing corrosion inhibition efficiency (Table 4 and Figure 4).

When comparing the level of coating (1, 3 and 5 days of PANI exposure), the maximum corrosion inhibition was seen in 5 day PANI exposure steel coupon (88.5%). Thus, the present study show that the 5 day PANI expose steel coupon have maximum corrosion inhibition rate (88.5%) against SR bacteria. The inhibition efficiency of the PANI nanofibre was decreased when they are exposed for long time duration. The decreasing level of corrosion rate and inhibition efficiency led to increase in the corrosion of steel by SR bacteria.

Conclusion

Corrosion is one of the most serious problems to the environment and to mankind. In this context, the present study aims to prepare an anti-corrosion agent such as PANI– nanofibre. The inhibition efficiency of the PANI-nanofibres coated steel coupons was studied with different day exposure of PANI- nanofibre for 1, 3 and 5 days. The PANI- nanofibre inhibits the corrosion level of the steel coupons induced by SRB. In this observation, the PANI- nanofibre coated steel coupons shows best results when compared with the sterile medium and SRB containing medium. This work will pave way for the uncorroded environment. Corrosion of the metals by sulphate reducing bacteria leads to serious problem to mankind that can be controlled by treating the steel coupons with PANI- nanofibres.

Conflict of interests

The authors did not declare any conflict of interest.

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