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Investigation of SRB induced biocorrosion of mild steel and its control

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Recently there has been a growing interest on biocorrosion of mild steel which is commonly used in ship ballast tank construction. Though prone to corrosion, mild steel finds abundance applications because of its inexpensive nature and ease of machinability. Biocorrosion caused by anaerobic bacteria causes significant damage and among the anaerobic population, sulfate reducing bacteria (SRB) tops the list. This study investigates the biocorrosion of mild steel by *Desulfovibrio desulfuricans* in neutral media. The use of bitter gourd extract as the corrosion inhibitor has been investigated using weight loss studies. The biotic media caused significant corrosion with a weight loss of 75.6 mg in 4 weeks immersion period. The use of 100 ppm bitter gourd extract was able to give about 94.4% inhibition efficiency against corrosion. The electrochemical studies also show similar trend like weight loss experiments.

Keywords: Mild steel, biocorrosion, bitter gourd, SRB, inhibition.

Introduction

Mild steel is commonly used metal because of its inexpensive nature and easy machinability. Oil transportation lines in refineries, headers in heat exchangers are some of the areas where mild steel is used extensively[1]. Among the microbial community causing material corrosion, anaerobic sulfuate reducing group popularly called as sulfate reducing bacteria (SRB) have been studied largely in view of the detrimental effects caused by their attack. There are many literature that investigated in detail the SRB influenced corrosion of different metals[2]. However, very less have been reported on the control of the same[3–5]. There are various options for the control of biocorrosion. Bioengineered microbial strains that produce antimicrobials have been reported by few groups. But the technique is highly sophisticated and the microbes failed to provide corrosion control in field trials[4]. Use of corrosion resistant coating has been found to be effective, however the effect did not last long when the coating presented discontinuities. Use of inhibitors which are organic chemicals that offer corrosion protection when added in small quantities is another promising technique to combat biocorrosion. However, most of the inhibitors are toxic and cause environmental pollution. This has made the search for new environmental friendly inhibitors of plant origin necessary. Extracts of neem leaf, onion and garlic have been studied as corrosion control inhibitors. However, only bacterial growth studies were made using such extracts. No corrosion studies have been made in detail. The use of inhibitors for biocorrosion control is less studied. This paper reports the use of bitter gourd extract to control the corrosion of mild steel corrosion caused by *Desulfovibrio desulfuricans*, a SRB commonly found in soil and refinery environment, in neutral media. The gravimetric and electrochemical studies have been used to study the biocorrosion.

Experimental

Mild steel coupons (1 cm×1 cm) were used for the corrosion studies. Before experiments, the coupons were polished with grit paper of various grades and cleaned well. Baar's medium was used as the growth medium the composition of which is shown in Table 1. The pH of the medium was adjusted to 7, before being used for the experiment.

The inhibitor extract was prepared by soaking the bitter gourd powder in ethanol for 24 h and refluxing the extract. The extract was concentrated using vacuum evaporation process and used. In this study 100 ppm of bitter gourd extract was used.

Table 1. Composition of the Baar's medium used for the experiments (for 1 L medium)

Chemicals	Mass (g)
$MgSO_4.7H_2O$	2.0
Calcium sulfate	2.0
NH_4Cl	1.0
K_2HPO_4	0.5
Sodium lactate 60%	7.0
Ferrous ammonium sulfate	0.5

The Baar's medium and all the containers along with metal coupons were autoclaved before use.

Throughout this paper, the nutrient media that contained only *Desulfovibrio desulfuricans* is referred to as "biotic-uninhibited" (BUI) and media with *Desulfovibrio desulfuricans* and 100 ppm bitter gourd extract is referred to as "biotic-inhibited" (BI). Pre-weighed mild steel coupons were immersed in different test tubes containing either BUI or BI media. The entire system is sealed properly and then incubated at 37°C. The coupons in the test tubes were taken out periodically to measure the weight loss. The weight loss of the coupons in BUI and BI media were calculated and the inhibition efficiency offered by the inhibitor was estimated using the formula provided below[5,6].

$$\mathrm{IE} = \frac{(W_{\mathrm{BUI}} - W_{\mathrm{BI}})}{W_{\mathrm{BUI}}} \times 100 \qquad (1)$$

where W_{BUI} and W_{BI} are the weight loss of the mild steel coupons in BUI and BI media respectively.

The electrochemical characterization studies were also carried out for the mild steel coupons immersed in BUI and BI media. Potentiodynamic polarization studies were carried out to calculate the corrosion current and potential. The mild steel coupons served as the working electrode, reference electrode was Ag/AgCl and platinum wire was the counter electrode.

For the third- and fourth-week samples, once the metal coupons were removed, the medium was tested for sulphide analysis in both inhibited and uninhibited cases. Sulfide was analysed using iodometry[7].

Results and discussion

Weight loss experiments:

The weight loss values of the mild steel coupons in BUI and BI media are presented in Table 1. Addition of the inhibitor extract has brought down the weight loss significantly. The weight loss values for the second week and fourth week of immersion are less when compared to the weight loss values of week 1 and 3 in both inhibited and uninhibited media. This is due to the change in the thickness of the biofilm or the corrosion products layer[5]. The biofilm or the corrosion products layer tends to grow with immersion period. Formation of such layer in uninhibited media is due to the metabolic activities of the SRB, which result in the formation of a layer comprising of corrosion products and metabolic products of bacteria. In the case of inhibited medium, a little metabolic activity of the bacteria and corrosive action of the medium contributes to external layer deposit. In both the cases the outer layer differs in composition and properties. These layers grow and when certain thickness is reached, there is no proper support for the layers from the substrate. This leads to the falling off the biofilm from the surface. Fig. 1 shows the scanning electron microscopy images of mild steel coupons in BUI media after one and two weeks of immersion. It is seen clearly that the morphology of the biofilm is different for both the samples. The sample immersed for one-week shows the presence of globular white zones and dark region. The dark region is somewhat continuous. The second week sample shows smaller white granular zones. Some bacteria are also visible in the images (shown by circles). Biofilm acts as a diffusion barrier for the corrosive media to attack the metal[6]. With the thickness variations, the corrosion intensity will change, thus causing a fluctuating weight loss. The inhibited samples present a very low weight loss with an average inhibition efficiency of 94.4%. The bitter gourd extract thus helps in the control of microbial corrosion of mild steel. It is believed that the inhibitor molecules adsorb on the metal surface and prevent the activity of the SRB[4].

Table 2 shows the sulfide analysis results of the media after three and four weeks of immersion of the mild steel coupons in uninhibited and inhibited cases. It is clear that the sulfide values are decreased significantly. Sulfide content drops to 80 ppm from 205 ppm for the third week and for the fourth week it decreases to 50 ppm as against the uninhibited sulfide content of 320 ppm. This shows that the inhibitor can decrease the bacterial activity but did not stop its growth completely.

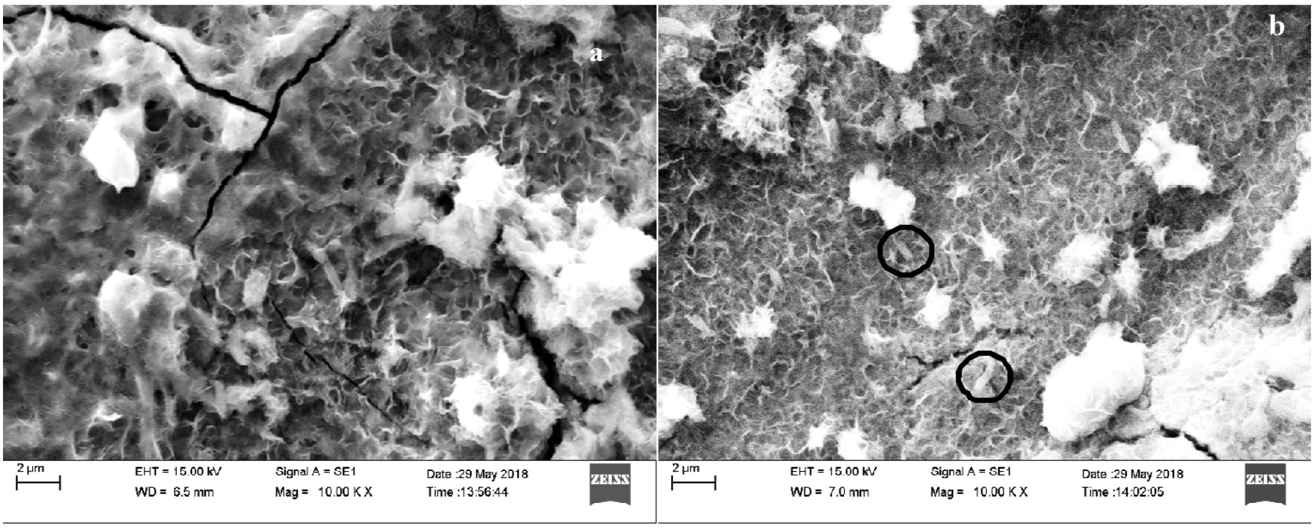

Fig. 1. Scanning electron microscopy images of mild steel coupons in BUI media: (a) first week and (b) second week.

Electrochemical experiments:

The results of potentiodynamic polarization experiments using mild steel coupons immersed in BUI and BI media after three weeks of immersion are shown in Fig. 1. The Tafel parameters for the same are shown in Table 2. The shape of the cathodic and anodic branches in both BUI and BI media are the same which indicates that the inhibitor does not alter the corrosion mechanism significantly.

Table 2. Weight loss results of the mild steel coupons in BUI and BI media at different immersion periods

Weeks	Weight loss (mg)		IE%	Sulfide concentration (ppm)	
	BUI	BI		BUI	BI
1	36.5	2.0	94.5	–	–
2	57.3	2.9	95.0	–	–
3	42.0	2.8	93.3	205	80
4	75.7	4.1	94.6	320	51

The cathodic and anodic Tafel lines are parallel for BUI and BI cases. This shows that the inhibitor does not significantly alter the cathodic hydrogen evolution and anodic metal dissolution reactions. However, the cathodic and anodic branches show decreased current density with the addition of inhibitor. The cathodic (β_c) and anodic (β_a) Tafel slopes in BUI and BI cases show a significant change in the β_a with inhibitor addition which shows that the anodic dissolution process is affected more with the addition of inhibitor. This shows that the inhibitor works by blocking the active reaction sites and inhibit the metal dissolution reaction of anode and the hydrogen evolution reaction of the cathode. The adsorbed inhibitor molecules also prevent the formation of biofilm on the metal surface thus decreasing the extent of corrosion[4]. The values of the polarization resistance and corrosion potential change drastically with inhibitor addition indicating corrosion control by bitter gourd inhibitor.

The corrosion current decreased from 261 µA to 8.5 µA upon inhibitor addition. The inhibition efficiency using the I_{corr} obtained from potentiodynamic polarization runs IE_{Taf} can be calculated using the formula mentioned below[7].

$$IE_{Taf} = (\Delta I_{corr})/I_{corr}^{0} \quad (2)$$

where ΔI_{corr} is the absolute difference in the I_{corr} values obtained from potentiodynamic polarization plots of BUI and BI media and I_{corr}^{0} is the corrosion current obtained from BUI media. The inhibition efficiency calculated from the I_{corr} values is 97% which matches well with the weight loss studies.

Table 3. Tafel parameters from potentiodynamic polarization plots of mild steel in BUI and BI media after three weeks immersion

Tafel parameters	BUI	BI
E_{corr} (V vs Ag/AgCl)	–0.65	–0.67
I_{corr} (µA)	261	8.5
R_p (Ω)	123	260
β_a (V/dec)	0.317	0.181
β_c (V/dec)	0.096	0.076

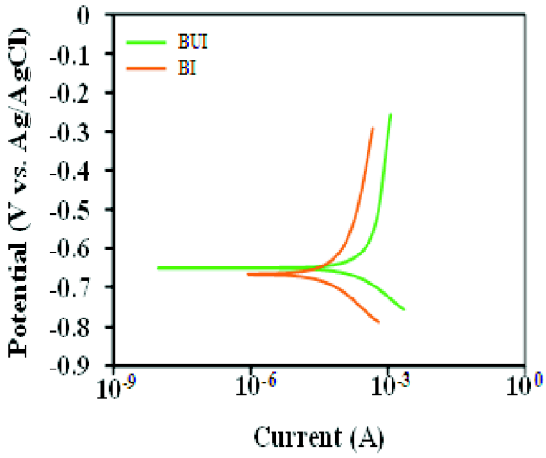

Fig. 2. Potentiodynamic polarization plots of mild steel coupons in different media after three weeks immersion.

The polarization resistance (R_p) for the system with inhibitor is higher (260 Ω) whereas, for the uninhibited medium it is 123 Ω. A lower resistance indicates the conditions favorable for corrosion in the absence of inhibitor. Thus, the bitter gourd extract helps to control SRB induced corrosion of mild steel in neutral medium.

Discussion:

The solvent used for inhibitor extract preparation from any plant material influence the composition of the extract. The ethanolic extract of bitter gourd has been shown to contain up to 20 mg GAE/g extract of total phenolics[7]. Apart from that bitter gourd extract is also a rich source of terpenoids, proteins and flavonoids[7]. Mass spectroscopic study of bitter gourd extract by Zhao *et al.*, showed the presence of momordicin alkaloids in significant quantities[8]. The terpenoids and alkaloids of bitter gourd possess antibacterial nature. It can be proposed that the bitter gourd extract acts in two ways: (i) by affecting the bacterial population by its antibacterial effect and (ii) by adsorption on to the metal surface to provide corrosion control. The sulfide analysis shows that the bacterial growth is not stopped completely, however a decrease in the bacterial activity is observed. Thus, the bitter gourd extract acts as a mild antibacterial agent. The potentiodynamic polarization studies indicate that the inhibitor molecules get adsorbed onto the metal surface thus blocking the active sites. The adsorption process helps in minimizing the corrosion caused SRB activity.

Conclusions

Use of bitter gourd extract to control the corrosion of mild steel caused by *Desulfovibrio desulfuricans* was studied.

The extract was found to provide 94.4% efficiency against the corrosion. The electrochemical results support the results obtained using weight loss studies.

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