

Full Length Research Paper

Corrosion behaviour of metals in artificial saliva in presence of spirulina powder

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Accepted 29 May, 2009

Corrosion resistance of three metals namely, SS 316L, mild steel (MS) and mild steel coated with zinc (MS-Zn) has been evaluated in artificial saliva in the absence and presence of spirulina. Potentiodynamic polarization study and AC impedance spectra have been used to investigate the corrosion behaviour of these metals. The order of corrosion resistance of metals in artificial saliva, in the absence and also in the presence of spirulina was SS 316L > MS > MS-Zn.

Key words: Artificial saliva, corrosion, metals, spirulina, dentistry, oral hygiene.

INTRODUCTION

In dentistry, metallic materials are used as implants in reconstructive oral surgery to replace a single teeth or an array of teeth, or in the fabrication of dental prosthesis such as metal plates for complete and partial dentures, crowns, and bridges, essentially in patients requiring hypoallergenic materials. Due to its mechanical properties, good resistance to corrosion in biological fluids and very low toxicity, titanium was the most commonly selected material for dental implants and prosthesis. Corrosion of metallic implants was of vital importance, because it can adversely affect the biocompatibility and mechanical integrity of implants. Many metals and alloys have been used in dentistry. Their corrosion behaviour in artificial saliva has been investigated. Influence of pH and corrosion inhibitors such as citric acid, sodium nitrate and benzotriazole on the tribocorrosion of titanium in artificial saliva has been investigated (Vieira et al., 2006). Five non-precious Ni-Co based alloys have been analyzed with respect to their corrosion behaviour in artificial saliva (Mareci et al., 2005). The effect of eugenol on the titanium corrosion in artificial saliva enriched with eugenol at different concentrations has been investigated by Kinani and Chtaini (2007). The corrosion resistance of the commercial metallic orthodontic wires in simulated intra-oral environment has been evaluated by Ziebowicz

et al, (2008). Results of corrosion resistance tests of the CrNi, NiTi and CuNiTi wires showed comparable data of parameters obtained in artificial saliva (Ziebowicz et al., 2008). The effects of multilayered Ti/TiN or single-layered TiN films deposited by pulse-biased arc ion plating (PBAIP) on the corrosion behaviour of NiTi orthodontic brackets in artificial saliva have been investigated by Liu et al, (2007).

Spirulina is a tiny aquatic plant, which has been eaten by human since prehistoric times. It was a vegetable with more protein than soy, more vitamin A than carrots and more iron than beef. It was low in fat, good for brain, heart and immune system. Spirulina is eaten by people in the form of biscuit, tablets etc. In the present study commercially available green spirulina powder was used. The present work was undertaken to study the corrosion behaviour of three metals, namely, mild steel, mild steel coated with zinc and SS 316L in artificial saliva, in the absence and presence of spirulina, by polarization study and AC impedance spectra. Corrosion parameters such as corrosion potential, corrosion current, linear polarization resistance, charge transfer resistance and double layer capacitance have been derived from these studies.

MATERIALS AND METHODS

Three metal specimens, namely, mild steel, mild steel coated with zinc (commercial) and SS 316L were chosen for the present study. The composition of mild steel was (wt%): 0.026 S, 0.06 P, 0.4 Mn,

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0.1 C and balance iron (Arockia Selvi et al., 2009). The composition of SS 316L was (wt%): 18 Cr, 12 Ni, 2.5 Mo, <0.03 C and balance iron (Gurappa, 2002). The metal specimens were encapsulated in Teflon. The surface area of the exposed metal surface was 0.0785 cm². The metal specimens were polished to mirror finish and degreased with trichloroethylene. The metal specimens were immersed in Fusayama Meyer artificial saliva (AS) (Kinani, 2007), whose composition was: KCl (0.4 g/l), NaCl (0.4 g/l), CaCl₂·2H₂O (0.906 g/l), NaH₂PO₄·2H₂O (0.690 g/l), Na₂S·9H₂O (0.005 g/l), urea (1 g/l). The pH of the solution was 6.5 (Hong et al., 2006).

In electrochemical studies, the metal specimens were used as working electrodes. Artificial saliva (AS) was used as the electrolyte (10 ml). The temperature was maintained at 37 ± 0.1 °C.

Commercially available spirulina powder was used in this study. 0.5 g of spirulina was dissolved in 1 litre of artificial saliva.

Potentiodynamic polarization

Polarization studies were carried out in a CHI – Electrochemical workstation with impedance, Model 660A. A three-electrode cell assembly was used. The working electrode was one of the three metals. A saturated calomel electrode (SCE) was the reference electrode and platinum was the counter electrode. From the polarization study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (anodic = b_a and cathodic = b_c) were calculated.

AC impedance spectra

The instrument used for polarization study was used to record AC impedance spectra also. The cell setup was also the same. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms at various frequencies. Values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated from Nyquist plots. Impedance log (Z/ohm) value was calculated from Bode plots.

RESULTS AND DISCUSSION

Analysis of potentiodynamic polarization curves

Corrosion behaviour of metals in artificial saliva: The corrosion parameters of various metals such as, mild steel, zinc coated mild steel and stainless steel 316L (SS), immersed in artificial saliva (AS) are given in Table 1. The potentiodynamic polarization curves are shown in Figures 1 - 3.

Mild steel (MS): When mild steel was immersed in artificial saliva (AS), the corrosion potential was -657 mV vs SCE (Figure 1a). The linear polarization resistance (LPR) was $2.06 \times 10^4 \text{ ohm cm}^2$ and the corrosion current (I_{corr}) was $1.98 \times 10^{-6} \text{ A/0.00785 cm}^2$.

Mild steel coated with zinc (MS-Zn): When zinc coated mild steel was immersed in AS, the corrosion potential shifted to the cathodic side (Figure 2a). The LPR value increased to $4.34 \times 10^4 \text{ ohm cm}^2$ and the corrosion current decreased to $9.98 \times 10^{-7} \text{ A/0.00785 cm}^2$ (Table 1). These observations indicated that zinc coated mild steel

was more corrosion resistant than mild steel itself. A protective layer was formed on the metal surface.

In the case of mild steel coated with zinc, the cathodic Tafel slope was 187 mV/decade and the anodic Tafel slope was 218 mV/decade. These values suggested that during anodic polarization, the rate of change of corrosion current with potential was high, and it was less during the cathodic polarization.

SS 316L: When SS 316L was immersed in AS, the corrosion potential was shifted to the noble side (-385 mV vs SCE) (Figure 3a). This suggested that a protective film was formed on the metal surface, when it was immersed in AS. The LPR value was very high $5.52 \times 10^{-6} \text{ ohm cm}^2$. The corrosion current decreased to a great extent. ($8.55 \times 10^{-9} \text{ A/0.00785 cm}^2$) (Table 1). The values of Tafel slopes ($b_a = 430$, $b_c = 145 \text{ mV/decade}$) indicated that the rate of change of current with potential was high during anodic polarization than during cathodic polarization. During cathodic polarization, current remained constant over a potential range.

A comparison of LPR values and corrosion current values of the three metals investigated revealed that SS 316 L was a better candidate to be used in dentistry.

Corrosion behaviour of metals in artificial saliva containing spirulina

Mild steel (MS): When mild steel was immersed in AS, containing spirulina, the corrosion potential was slightly shifted to the cathodic side (when compared with the behaviour of mild steel in AS) (Figure 1b). The Tafel slopes were not affected very much. However, it was observed that the cathodic Tafel slope was slightly influenced. It was interesting to note that in the presence of spirulina, the LPR value increased and the corrosion current decreased. It seems that a protective layer was formed on the metal surface which controlled the rate of corrosion of mild steel in AS, in the presence of spirulina.

Mild steel coated with zinc (MS-Zn): When mild steel coated with zinc was immersed in AS, containing spirulina, the corrosion potential was shifted to -809 mV vs SCE (Figure 2b). That is corrosion potential was shifted to anodic side in presence of spirulina (when compared to the corrosion potential in the absence of spirulina). Both the Tafel slopes were influenced in the presence of spirulina. The Tafel slopes were: $b_c = 220 \text{ mV/decade}$ and $b_a = 194 \text{ mV/decade}$. That is, rate of change of corrosion current in the anodic region was less when compared with that in the cathodic region. It is interesting to note that in the presence of spirulina, the LPR value decreased (from 4.34×10^4 to $2.45 \times 10^4 \text{ ohms cm}^2$) and the corrosion current increased (from 9.98×10^{-7} to $1.826 \times 10^{-6} \text{ A/0.00785 cm}^2$). That is, in the presence of spirulina, the corrosion resistance of mild steel coated with zinc decreased.

Table 1. Corrosion parameters of metals immersed in artificial saliva (SA) in the absence and presence of spirulina, obtained by polarization study.

Metal	System	E_{corr} mV vs SCE	b_c mV/decade	b_a mV/decade	LPR ohm cm^2	I_{corr} A/0.00785 cm^2
MS	AS	-657	278	142	2.057×10^4	1.983×10^{-6}
	AS + Spirulina	-725	286	146	5.275×10^4	7.970×10^{-7}
MS-Zn	AS	-855	187	213	4.340×10^4	9.976×10^{-7}
	AS + Spirulina	-809	220	194	2.452×10^4	1.826×10^{-6}
SS	AS	-385	145	430	5.518×10^6	8.551×10^{-9}
316L	AS + Spirulina	-391	140	442	6.204×10^6	7.411×10^{-8}

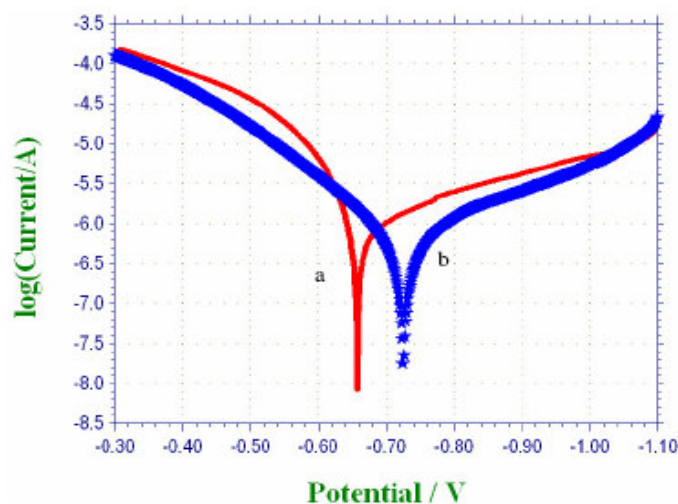


Figure 1. Polarization curves of MS immersed in various test solutions

AS
AS + spirulina

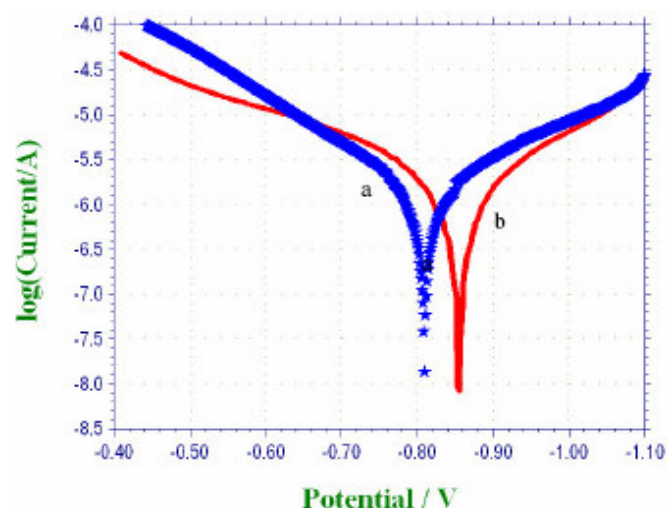


Figure 2. Polarization curves of MS-Zn immersed in various test solutions.

AS
AS + spirulina

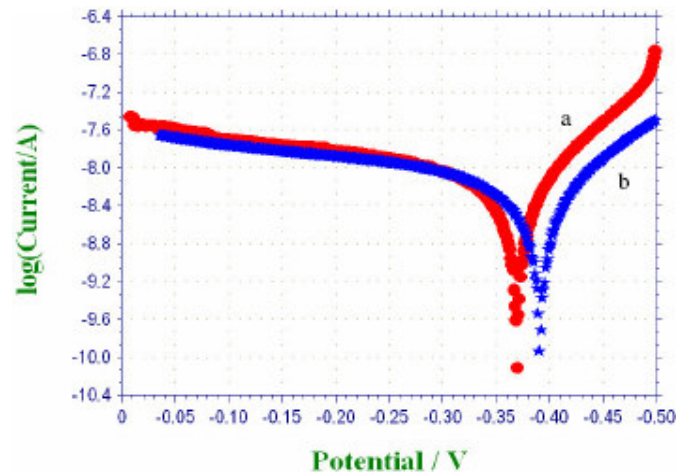


Figure 3. Polarization curves of SS 316L immersed in various test solutions.

AS
AS + spirulina

SS 316L: In the presence of spirulina, the corrosion resistance of SS 316L in artificial saliva increased. This was revealed by the increase in LPR value (from 5.52×10^6 to 6.20×10^6 ohm cm^2) and decrease in corrosion current (from 8.55×10^{-9} to 7.45×10^{-9} A/0.00785 cm^2). The corrosion potential was not changed very much. The Tafel slopes were not influenced very much (Figure 3b). Thus polarization study has led to the conclusion that in the presence of spirulina, the corrosion resistance of Mild steel in artificial saliva slightly increased. Mild steel coated with zinc in artificial saliva slightly increased. SS 316L in artificial saliva increased.

AC impedance spectra: AC impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) (derived from Nyquist plots) and impedance value $\log(z/ohm)$ (derived from Bode plots), of various metals immersed in artificial saliva and artificial saliva containing spirulina are given in Table 2. The AC impedance spectra are shown in Figures 4 to 6 (Nyquist plots) and Figures 7 to 12 (Bode plots).

Table 2. Corrosion parameters of metals immersed in artificial saliva (AS) in the absence and presence of spirulina obtained from AC impedance spectra

Metal	System	Nyquist plot		Bode plot
		R_t ohm cm^2	C_{dl} $\mu F/0.00785\text{ cm}^2$	Impedance $\log(z/ohm)$
MS	AS	779	6.54×10^{-9}	2.92
	AS + Spirulina	551	9.25×10^{-9}	2.75
MS-Zn	AS	650	7.84×10^{-9}	2.82
	AS + Spirulina	843	6.05×10^{-9}	2.96
SS 316L	AS	29577	0.17×10^{-9}	4.72
	AS + Spirulina	27703	1.84×10^{-10}	4.70

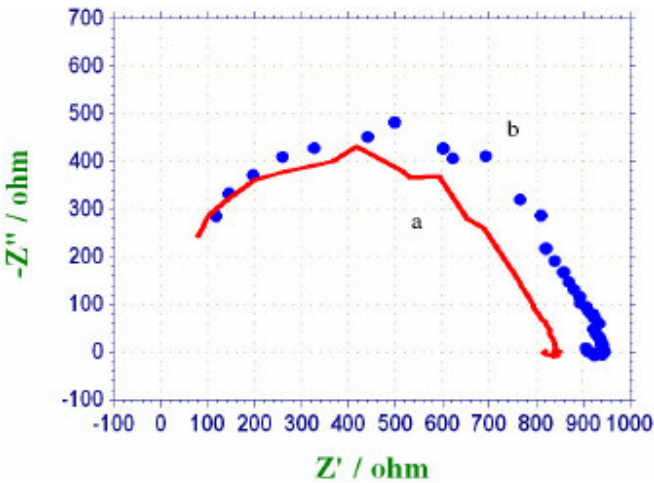


Figure 4. AC impedance spectra (Nyquist plots) of MS immersed in various test solutions.

AS
AS + spirulina

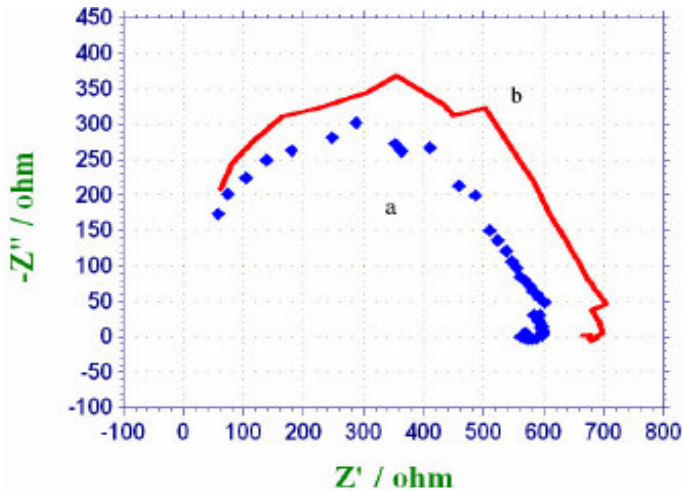


Figure 5. AC impedance spectra (Nyquist plots) of MS-Zn immersed in various test solutions.

AS
AS + spirulina

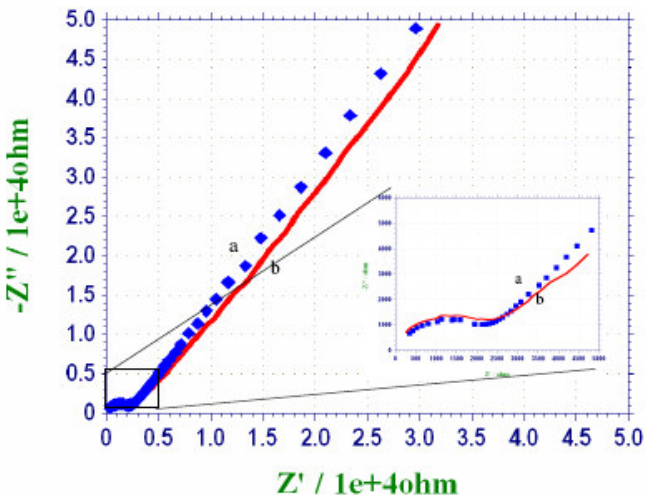


Figure 6. AC impedance spectra (Nyquist plots) of SS 316L immersed in various test solutions.

AS
AS + spirulina

Mild steel (MS): When mild steel was immersed in AS, (Figure 4a) the charge transfer resistance was 779 ohm cm^2 . The double layer capacitance was $6.54 \times 10^{-9} \mu F/0.00785\text{ cm}^2$. The impedance value ($\log(z/ohm)$) was 2.92 (Figure 7). In presence of spirulina, (Figure.4b), R_t value increased and C_{dl} value decreased. There was increase in the value of impedance ($\log(z/ohm)$) (Figure 8). These observations indicated that in the presence of spirulina in artificial saliva, the corrosion rate of mild steel was reduced, due to the formation of protective film formed on the metal surface. The protective film, probably, consisted of oxides of iron and iron complexes of the active principles present in spirulina.

Mild steel coated with zinc (MS-Zn): When mild steel coated with zinc was immersed in AS, the charge transfer resistance was 650 ohm cm^2 (Fig.5a). The double layer capacitance was $7.84 \times 10^{-9} \mu F/0.00785\text{ cm}^2$. The impedance value $\log(z/ohm)$ was 2.82. When these values are compared with the values of mild steel, it was obser-

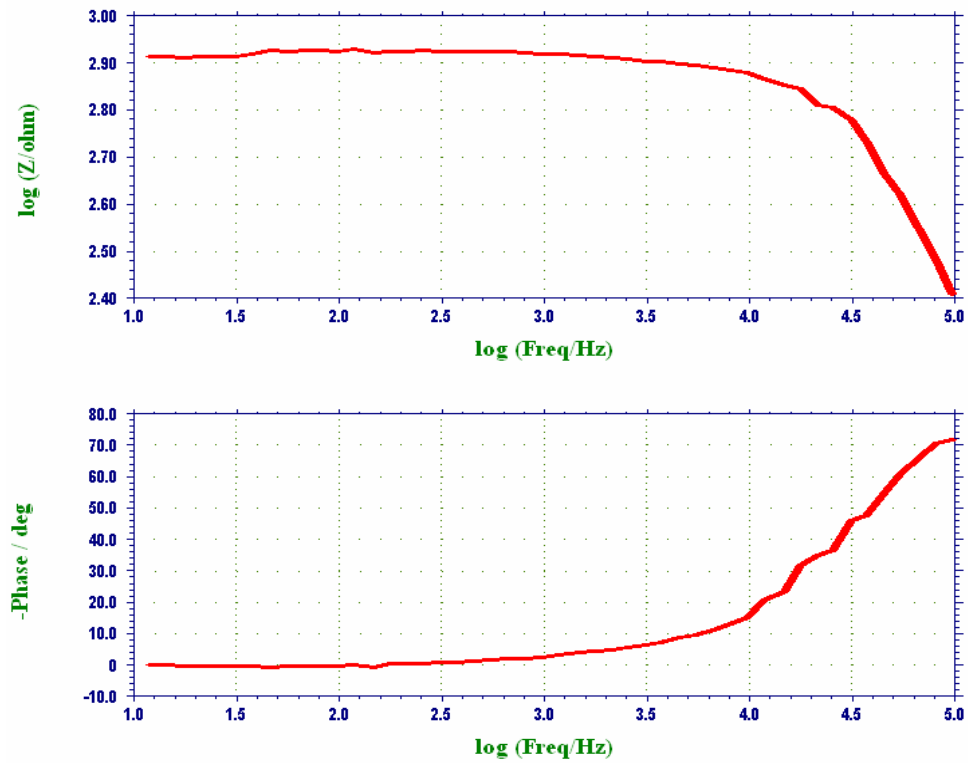


Figure 7. AC impedance spectra (Bode plots) of MS immersed in artificial saliva.

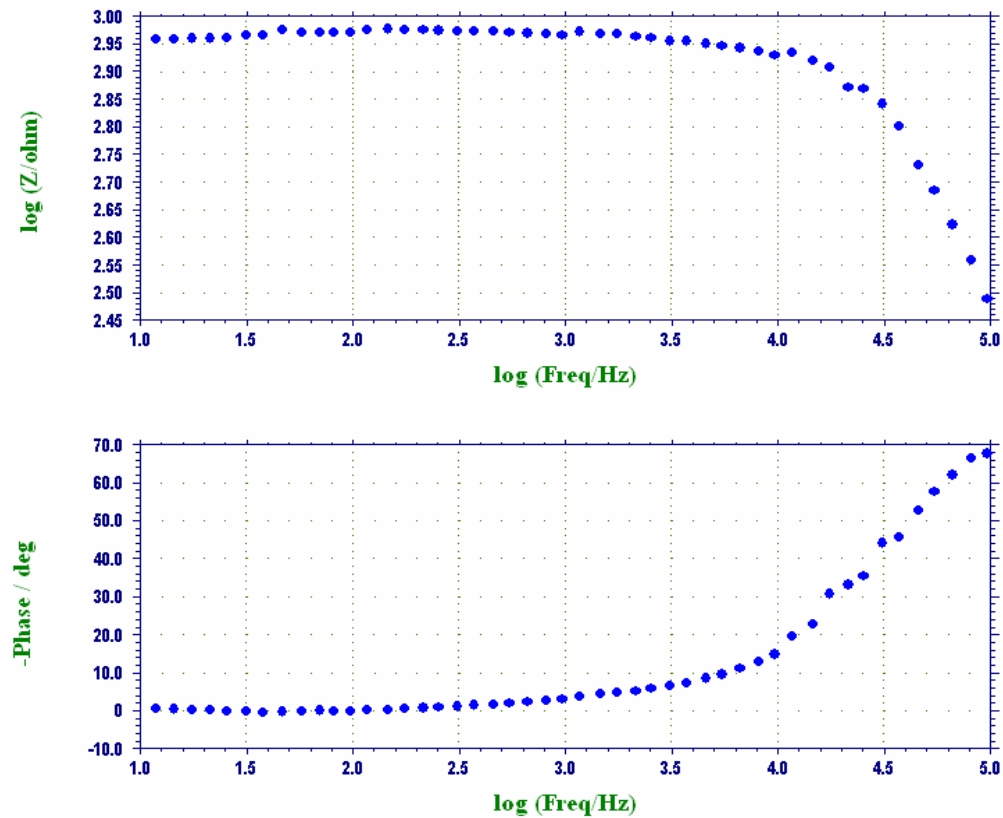


Figure 8. AC impedance spectra (Bode plots) of MS immersed in AS + spirulina.

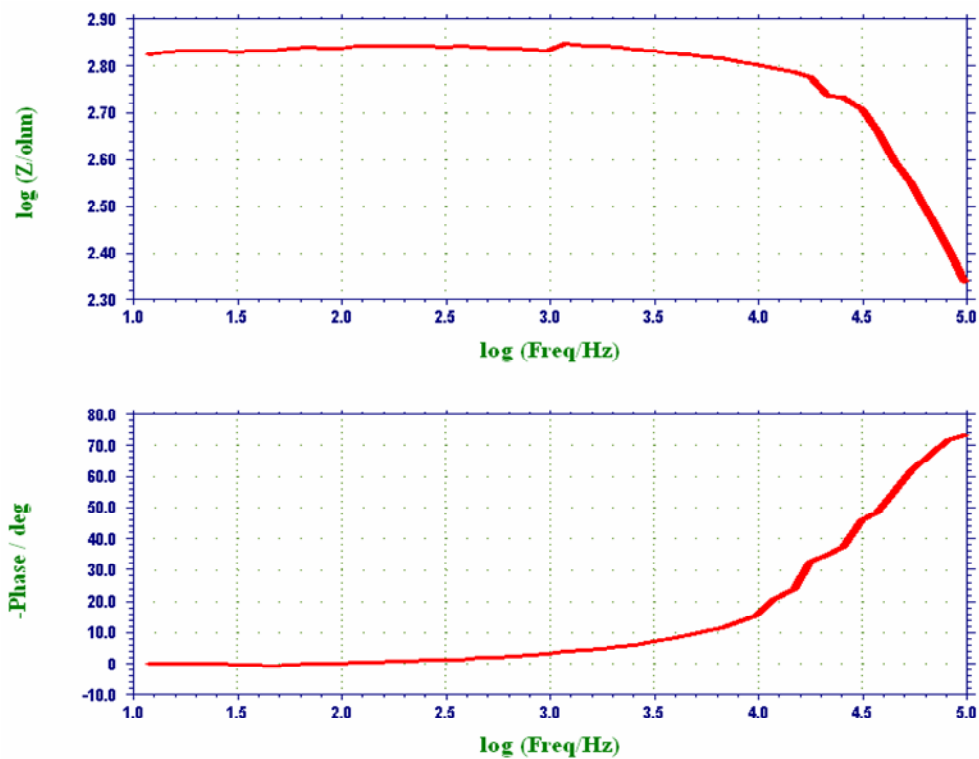


Figure 9. AC impedance spectra (Bode plots) of MS-Zn immersed in artificial saliva (AS).

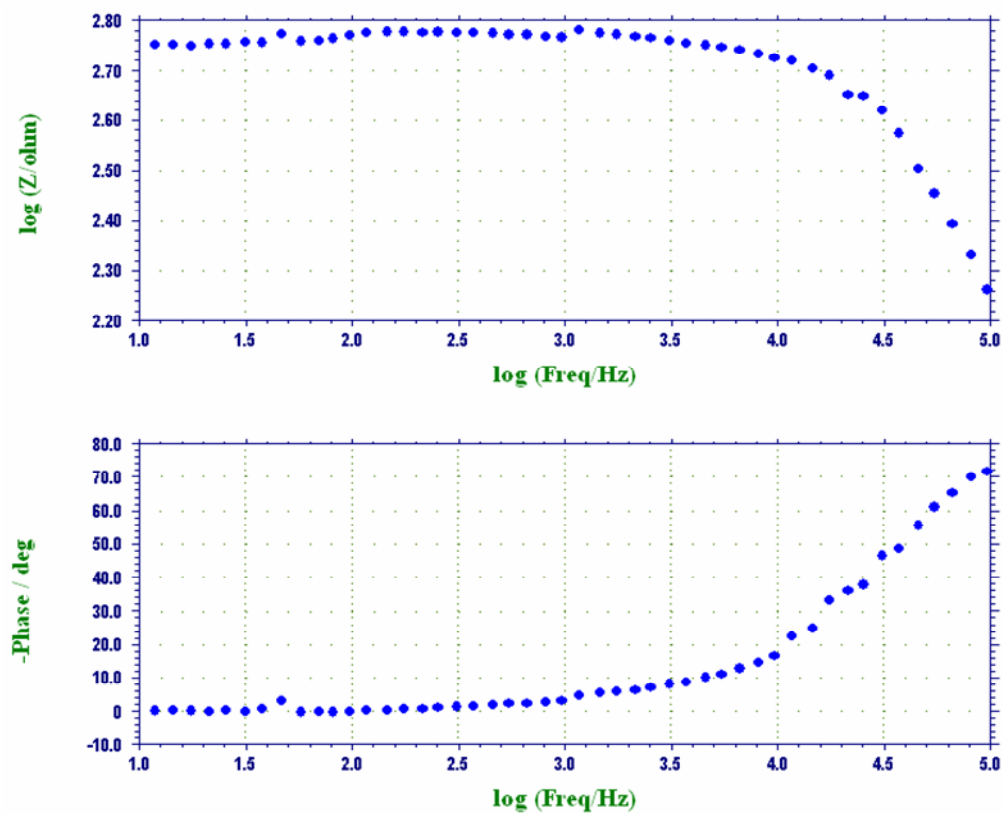


Figure 10. AC impedance spectra (Bode plots) of MS-Zn immersed in AS + spirulina.

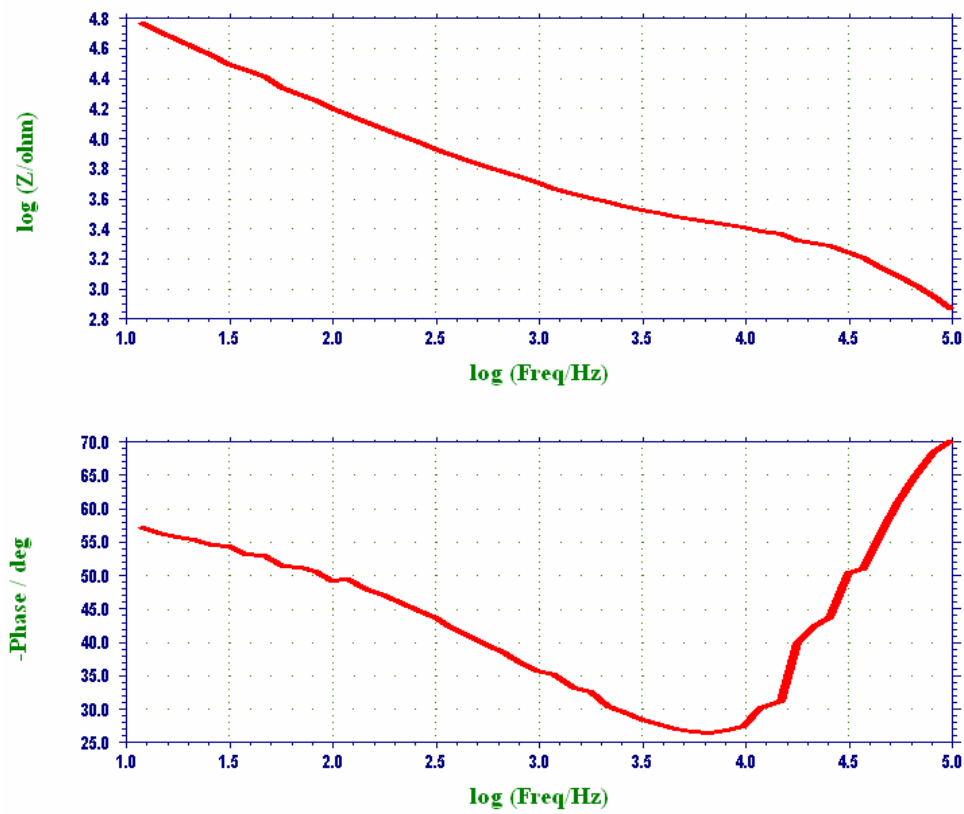


Figure 11. AC impedance spectra (Bode plots) of SS 316L immersed in Artificial Saliva.

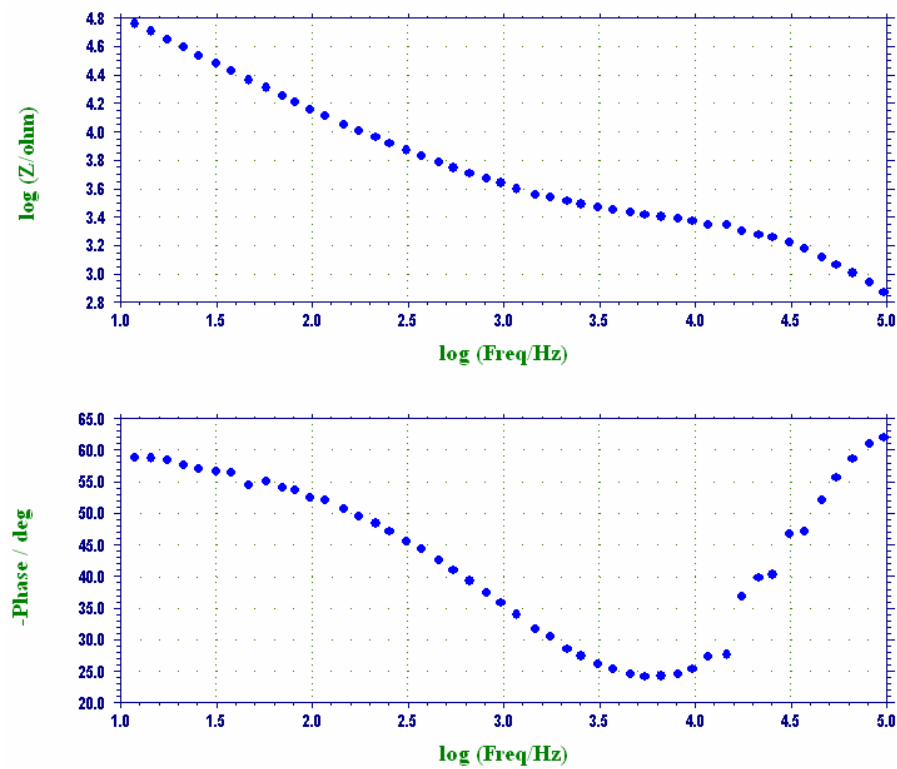


Figure 12. AC impedance spectra (Bode plots) of SS 316L immersed in AS + spirulina.

ved that mild steel coated with zinc was less corrosion resistant (in artificial saliva) than mild steel. That is the protective film formed on the metal surface was less stable and easily broken by the ions present in AS.

Similar observation was made when mild steel coated with zinc was immersed in AS containing spirulina (Figure 5b). The R_t value decreased from 843 to 551 ohm cm^2 ; the C_{dl} value increased from 6.05×10^{-9} to $9.25 \mu\text{F}/0.00785 \text{ cm}^2$; and the impedance value, $\log(z/\text{ohm})$, decreased from 2.96 to 2.75. This observation suggested that the film formed on mild steel coated with zinc in AS, in the presence of spirulina was less stable and easily broken by the ions present in AS.

SS 316L: When SS 316L was immersed in AS, the charge transfer resistance was very high, 29577 ohm cm^2 . The double capacitance was very low, $0.17 \times 10^{-9} \mu\text{F}/0.00785 \text{ cm}^2$; and the impedance value $\log(z/\text{ohm})$ was high, 4.72. These observations suggest that the protective film formed on SS 316L was more stable. It was able to withstand the attack of aggressive ions present in AS. SS 316L is a better candidate in artificial saliva, since it is more corrosion resistant, when compared with mild steel and mild steel coated with zinc.

When SS 316L was immersed in AS containing spirulina the R_t value was 27703 ohm cm^2 ; the C_{dl} value was $1.84 \times 10^{-10} \mu\text{F}/0.00785 \text{ cm}^2$; and impedance value, $\log(z/\text{ohm})$ was 4.70. These values suggested that in the presence of spirulina in AS, the corrosion resistance of SS 316L decreased. However it was more corrosion resistant than MS and MS coated with zinc, when they were immersed in AS in presence of spirulina.

Thus, AC impedance spectra have led to the conclusions that in the presence of spirulina, the corrosion resistance of mild steel in artificial saliva slightly increased. Mild steel coated with zinc in artificial saliva slightly decreased. SS 316L in artificial saliva decreased.

Conclusions

The corrosion behaviour of three metals namely, mild steel (MS), mild steel coated with zinc (MS-Zn) and SS 316L have been studied in artificial saliva in the absence and presence of spirulina. Polarization study has led to the following conclusions.

In the absence of spirulina, the order of corrosion resistance was:

$$\text{SS 316L} > \text{MS} - \text{Zn} > \text{MS}$$

In the presence of spirulina, the order of corrosion resistance was

$$\text{SS 316 L} > \text{MS} > \text{MS} - \text{Zn}$$

- SS 316L was more corrosion resistant in the presence of spirulina than in its absence.

- MS was more corrosion resistant in the presence of spirulina than in the absence of spirulina.
- MS-Zn was more corrosion resistant in the absence of spirulina than in the presence of spirulina.

AC impedance spectra have led to the following conclusions : In the absence of spirulina, the order of corrosion resistance was:

$$\text{SS 316L} > \text{MS} > \text{MS-Zn}$$

In the presence of spirulina, the order of corrosion resistance was

$$\text{SS 316 L} > \text{MS} > \text{MS} - \text{Zn}$$

- SS 316L was more corrosion resistant in the absence of spirulina than in the presence of spirulina.
- MS was more corrosion resistant in the presence of spirulina than in the absence of spirulina.
- MS-Zn was more corrosion resistant in the absence of spirulina than in the presence of spirulina.

ACKNOWLEDGEMENTS

The authors are thankful to their management, St. Joseph's Research and Community Development Trust, Dindigul and to the University Grants Commission, India, for their help and encouragement.

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