CORROSION OF 304 SATAINLESS STEEL IN SALINE SOLUTIONS CONTAINING THE CAROTENOID ALGA DUNALIELLA SALINA

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Abstract

The corrosion of 304 stainless steel in concentrated saline solutions containing the carotenoid alga DS has been studied by different techniques. The results of open circuit potential, potentiodynamic polarization and atomic absorption analysis of the test solution after immersion, accord. This alga inhibits the corrosion process by secreting β- carotene which adsorbs chemically on the corroding surface.

Introduction

Owing to the corrosion resistance of type 304 stainless steel, it has been used as a construction material in chemical industries where severe conditions are encountered, e.g., extraction of salts from natural waters (1). The corrosion resistance of this steel is due to the formation of a passive film (2). This film is susceptible to localized attack and pitting by chloride (3). In natural saline water some types of micro-organisms survive, e.g., the carotenoid alga Dunaliella Salina (4).

Studies dealing with corrosion of 304 stainless steel are numerous with regard to its, alloying, surface modification, coating, inhibition, pitting and stress corrosion cracking (5 -10), however, bio-corrosion measurements are fewer. The present article deals with corrosion of 304 stainless steel in saline solution containing the carotenoid alga Dunaleilla Salina.

This alga is unicellular and belongs to the class Chlorophyceae and the order Vlovocales. It is found naturally in many

aquatic marine habits containing more than 10% salt, e.g., Qu'aron lake's concentrated water. This lake (South Cairo) is hypersaline and the Dunaliella strain which predominates in its concentrated water is Dunaliella Salina (11). It is ovoid, motile and halotolerant via an osmoregulaion mechanism. It is of a commercial interest because it accumulates massive amounts of the precise compound β-carotene(12). Lacking a cell wall but a mucus surface coat, it responds easily to external tensions by secreting glycerol and β-carotene. It perforates only in sunlight(13).

Experimental

This study was undertaken with pure culture of the strain Dunaliella Salina. The media was prepared by the sequential addition of 130 g of NaCl, 35 g of Na_2SO_4 and 36.1 g of $MgSO_4 .7H_2O$ to less than 1 l of distilled water. It was then boiled, after that cooled to room temperature. The minor components; urea, potassium dihydrogen phosphate, iron-EDTA and sodium bicarbonate were added to give the recommended final concentrations; 0.1, 0.2, 0.002 and 2.0 mM, respectively(14). At last the solution was completed to 1 l with distilled water.

The crop of Dunaliella Salina was supplied from SRI, China. 0.25 l of this solution with cell number $1.5x10^5$ cell / ml was added to every 1 l of the media in a tank. It was kept under net shade exposed to sun light and moved to a cool place when the air temperature exceeds 35 °C and vice versa. It was shaken once an hour during the day time. This culture was diluted with proper amounts of the medium according to the growth rate so that the volumetric cell number does not exceed $2x10^6$ cell/ ml. Also it was diluted with distilled water to compensate evaporation for keeping the salinity constant (12). The alga produce β-carotene which can reach about 20 ppm in the culture solution. Under this condition the color of the solution becomes orange. The growth rate and β-carotene content were measured every day. The result are shown in Fig.(1).

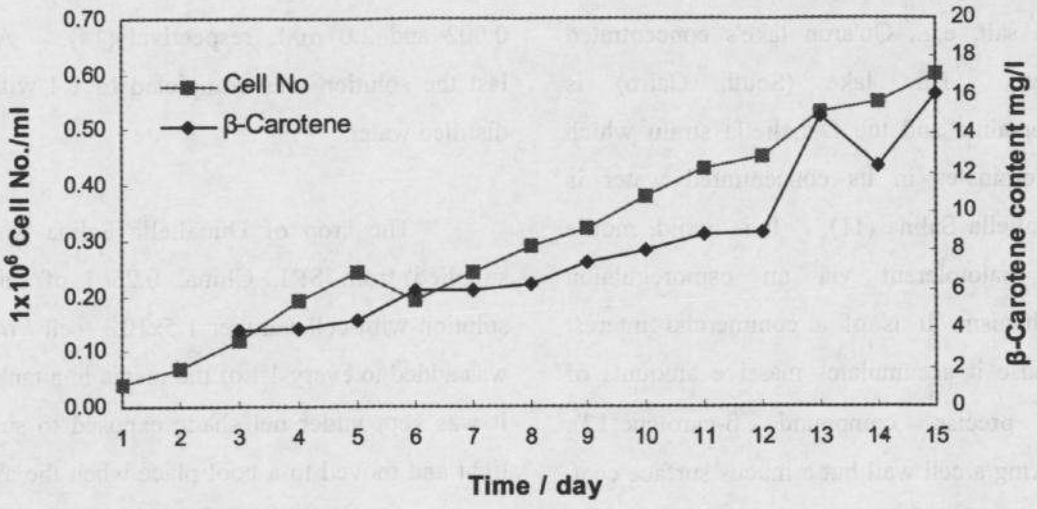

Fig. 1 Increase of cell no. and β-carotene content with growth time

The test electrode was prepared from commercial 304 stainless steel speciment supplied by Membrane Co. Italy . It has the composition given in Table (1).

Table 1. Chemical composition of the tested steel (the balance is iron)

Element	C	Si	Mn	P	S	Cr	Ni	Ti
%	0.06	0.53	0.21	0.025	0.016	17.45	9.8	0.57

It has been used in the form of a rod with diameter 0.53 cm and length 1.5 cm. Only one cross sectional end area was exposable to the test solution. A stout copper wire was fixed mechanically at the other end of the specimen. It was then fixed into a glass tube of appropriate internal diameter with a thin layer of an epoxy resin. Before each experiment the exposed electrode area was mechanically polished with fine emery paper from 400 to 1000 till a bright smooth surface with a silver mirror appearance has been obtained. Then it was rinsed with distilled water, after that dried with a fine filter paper and immediately immersed in a cell filled with a fresh portion of the test solution. The cell is a conventional three compartments electrochemical one.

The test solution has the composition of the medium mentioned. It has a pH of 8.7, naturally aerated and constantly mechanically stirred during measurements. Measurements were made in the laboratory (without the direct exposure to sun light) at 25 °C.

Saturated calomel electrode and platinum wire have been used as the reference and auxiliary electrodes, respectively. All potentials given here are relative to this reference. Potentiodynamic polarization measurements were made at a scan rate of 3 mV/s. A PAR potentiostat model 273/81 was used. It was electronically controlled by EG & G soft ware 252/352 corr II.

At the end of each electrochemical run (about two hours), the test solution was quantitatively analyzed with respect to the dissolved corrosion products, namely, Fe, Cr and Ni using GBC plus 932 atomic absorption spectrophotometer (15).

Results and Discussion

The open circuit potential, E, shifts towards the more positive direction with time, t, as shown in figure 2. The shift of E towards the positive direction increases with cell number, which means that the thick of passive film is higher in presence of the alga (16). E increases with time obeying a logarithmic rate law, Figs.2. This to be due to growth of the pre immersion film is by a dissolution precipitation mechanism (17). Furthermore, the rate of film growth is higher in the alga containing solution compared to the free one as revealed from the over all change in E; ε. It is defined as $(E_f - E_i) / \tau$, where E_f is the measured E after 90 min., E_i is the measured E after 10 seconds and τ = 975seconds, Fig.4. ε can be considered as thickening coefficient .

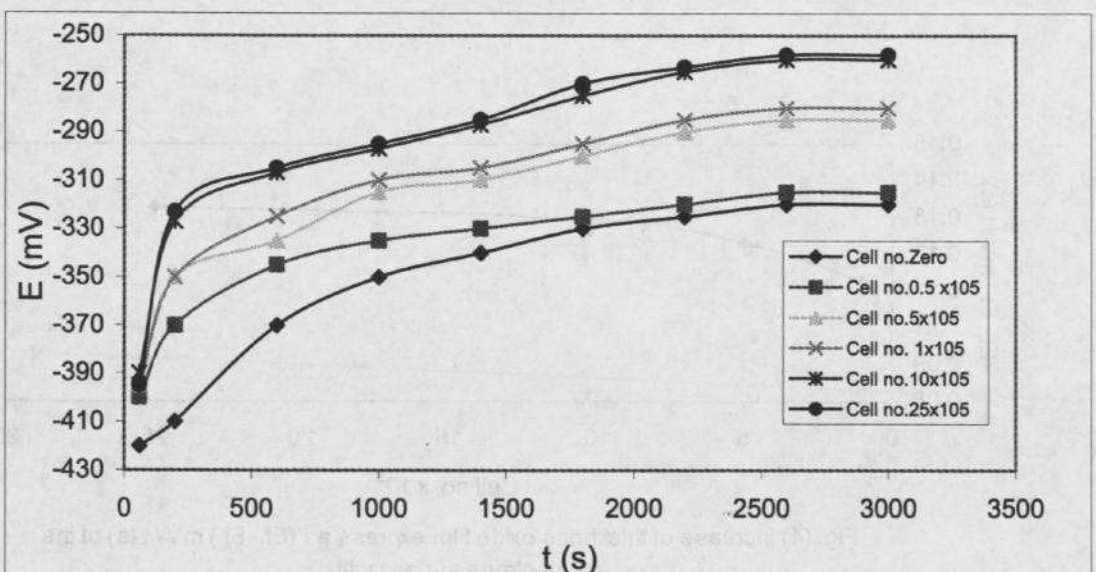

Fig. (2) change of the open circuit potential (E) of the electrode with immersin time (t) in absent and different addation of the alga.

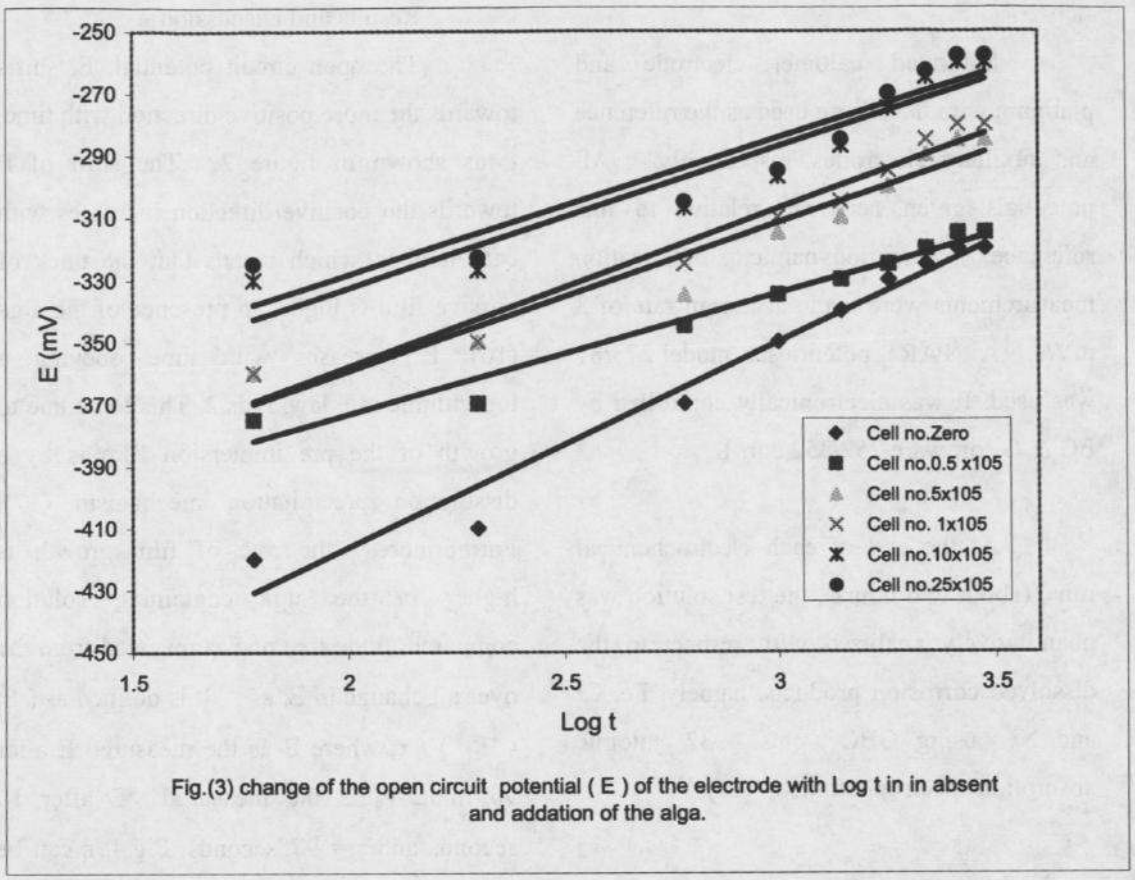

Fig.(3) change of the open circuit potential (E) of the electrode with Log t in in absent and addation of the alga.

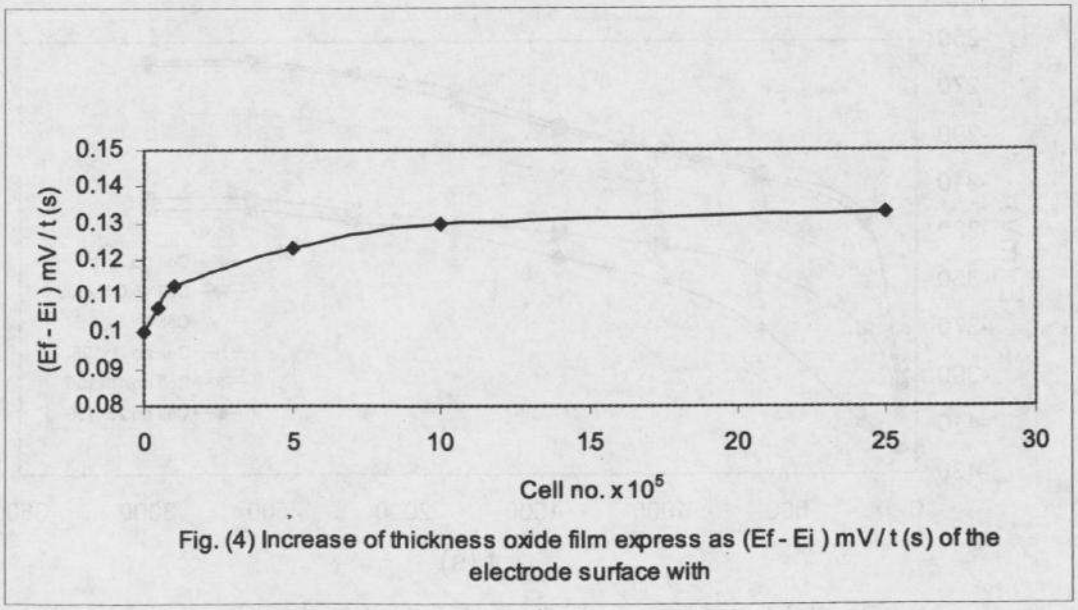

Fig. (4) Increase of thickness oxide film express as (Ef - Ei) mV / t (s) of the electrode surface with

The enhancement of the growth rate of the film in the presence of the alga can be attributed to different factor its adsorption on the electrode surface, meanwhile it secretes β-carotene and glycerol and produces oxygen gas. Adsorption of the alga is

suggested on account of the visual observation of accumulation of a yellow to orange coloration around the electrode. This supporting has confirmed by counting the cell number close to the electrode surface (by a slicing technique). The results reveal a higher value compared to the bulk solution (about 10 %). This conclusion has achieved by analyzing the surface biofilm layer with respect to chlorophyll a,b and c with 90 % acetone extracted, measurement of the absorbance has be read by Lambda 2 Perkin Elmer spectrophotometer , the result are given table (2) .

Table 2. Concentration of the chlorophyll a,b and c as well as the β-carotene in the biofilm formed on 304 stainless steel and the respective bulk values in solution containing different cell numbers.

Cell no./ml	Chlorophyll, mg/m^2			β- carotene, mg/l bulk /surface
	A bulk /surface	B bulk /surface	C bulk /surface	
$5x10^4$	0.27 / 0.30	0.18 / 0.19	0.19 / 0.21	1.6 / 1.75
$1.0x10^5$	0.56 / 0.62	0.37 / 0.42	0.5/ 0.51	3.2 / 3.5
$2.5x10^5$	0.85 / 1.0	0.44 / 0.50	0.6 / 0.66	8.0 / 9.0

The enhancement of the growth rate of the film in presence of the alga can be attributed to its hanging to the electrode surface and / or adsorption of the β-carotene it secretes (11). Hanging of the alga is suggested on account of the visual observation of accumulation of a yellow to orange coloration around the electrode. Counting the cell number close to the electrode surface by slicing the solution reveals higher values compared to the bulk solution (about 10%). The technique employed is analysis of bioflim layer with respect to chlorophyll a,b and c with extracted 90% acetone (12). Measurement of the absorbance has been made by Lambda 2 Perkin Elmer spectrophotometer, the are givin in table (2), the table contain also the β-carotene content in the same solution.

On the other hand the enhancement of the rate of film growth in presence of the alga could be due to the increase of oxygen concentration as a result of the photosynthesis process by the scattered sun light (18), as revealed from the increase in the amount oxygen (table 3)

Table (3) Oxygen dissolved measurements

Cell no. x104	0.0	5.0	10.0	25.0
O2 mg /l	7.8	8.5	9.5	11.5

This alga respond to external tensions by secreting β-carotene and glycerol (11). Secretion of these substances from alga is due to the electrode surface, which disturbs environment of the alga because generally any surface has active potential (19). Therefore the adsorption of these substances β-carotene should not be excluded. To confirm this scenario, in separate experiments, β-carotene and glycerol were extracted (12) from the cell and the effluence of it as well as the glycerol and the cell after extraction of β-carotene were examined. It has been fund that the effluence of β-carotene is compared to the whole cell regarding the inhibition of corrosion of 304 stainless steel. This conclusion has been confirmed by corrosion current measurements and chemical analysis of test solution as shown below.

The inhibitive action of the alga has been elucidated using the potentiodynamic polarization technique (19). Typical potentiodynamic curves are shown in figure (5). The curves are qualitatively similar. Thus it seems that the alga does not affect the mechanism of corrosion, since, the presence of the alga shifts the polarization curve towards the more positive direction. Furthermore the corrosion current decrease, figure (6). Therefore the role of the alga is liable to be a decrease in the exposed electrode area. Thus this alga affects the corrosion process by an adsorption mechanism, either the adsorption of the whole alga and the (hanging to the electrode surface) or via its metabolic products.

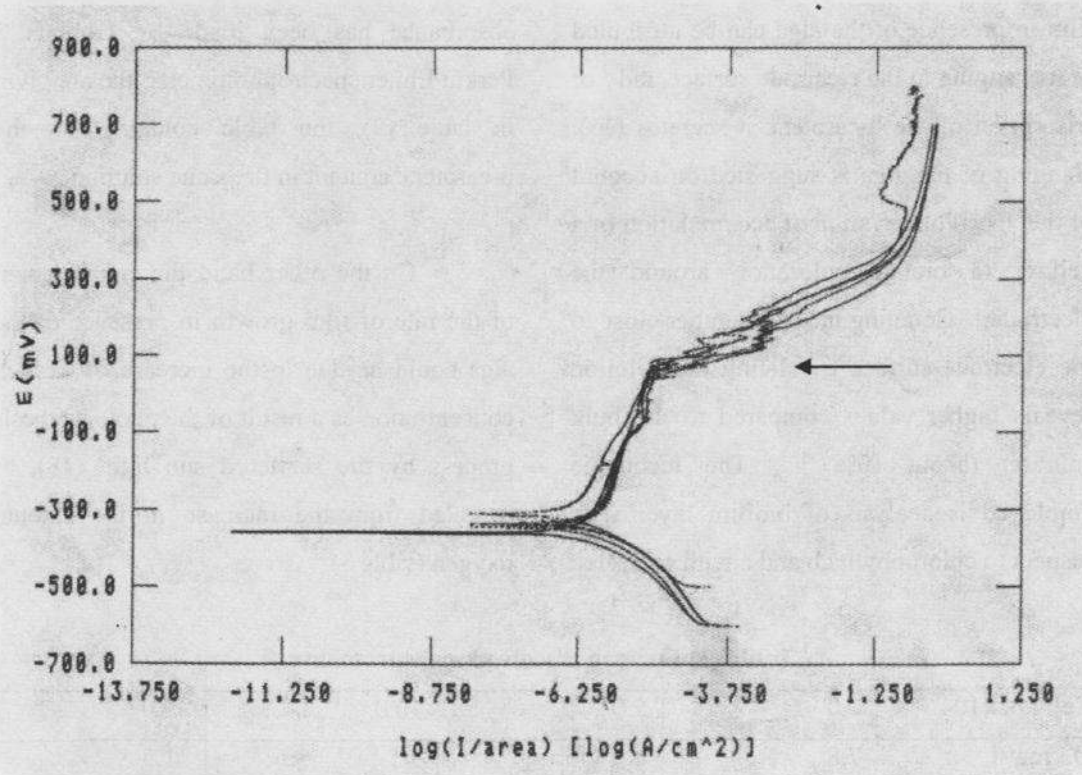

Fig .5 Poteniodynamic polarization curves at scan rate of 3 mV s-1 :from Free solution and in presence of series cell no. of alga up to 2.5x105 cell/ml)

This figure shown the effect of cell number of the potentiodynamic curve. The presence of the alga shift the corrosion potential toward the more positive direction, figure (5b). And the corrosion current decrease as shown in figure (5c). The inhibition effect of the alga has been confirmed for the observed parallel decrease in the corrosion of the dissolved corrosion product Figure (6). The represented inhibition effect observed of the alga has been attributed to the adsorption of secreted β carotene. Therefore β carotene has been extracted and tested as an addition for inhibition of corrosion of 304 stainless steel. The results are shown in figures (7a, 7b and 7c)

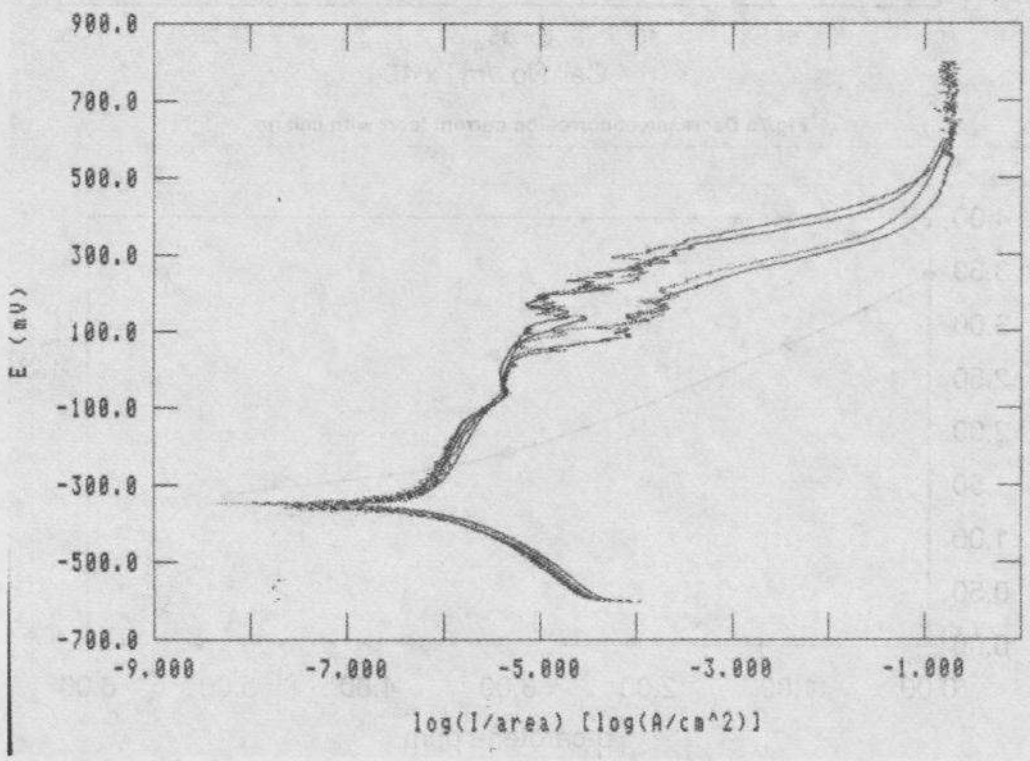

Fig .5b Poteniodynamic polarization curves at scan rate of 3 mV s-1 : from Free solution and in presence β-carotene up to 8ppm)

The corrosion current ,I , changes with the cell number ,N , and β-carotene as shown in figure (7 a and b). On the other hand the concentrations of the dissolved corrosion products in the test solutions after the runs change with N and β-carotene as shown in figure (8a1,2 and b1,2). These results accord phenomenological as shown in figure (9)

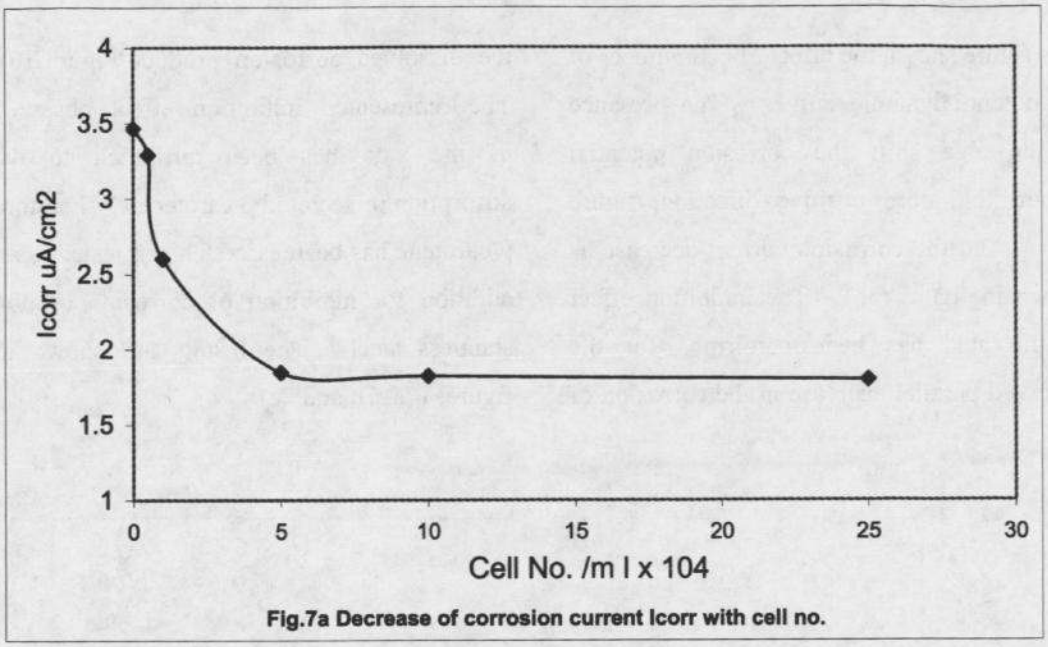

Fig.7a Decrease of corrosion current Icorr with cell no.

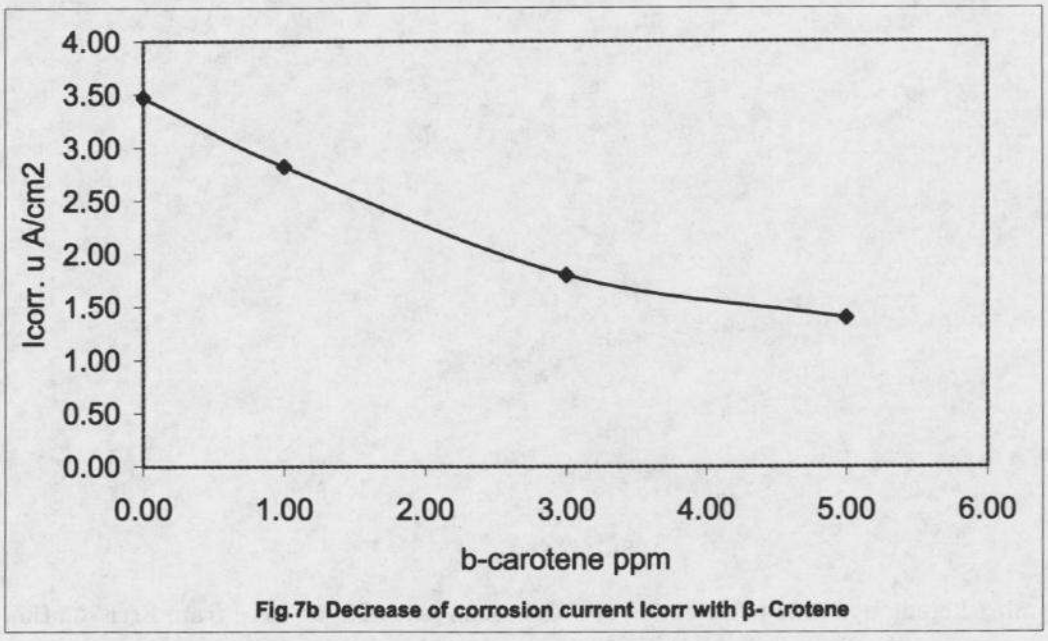

Fig.7b Decrease of corrosion current Icorr with β- Crotene

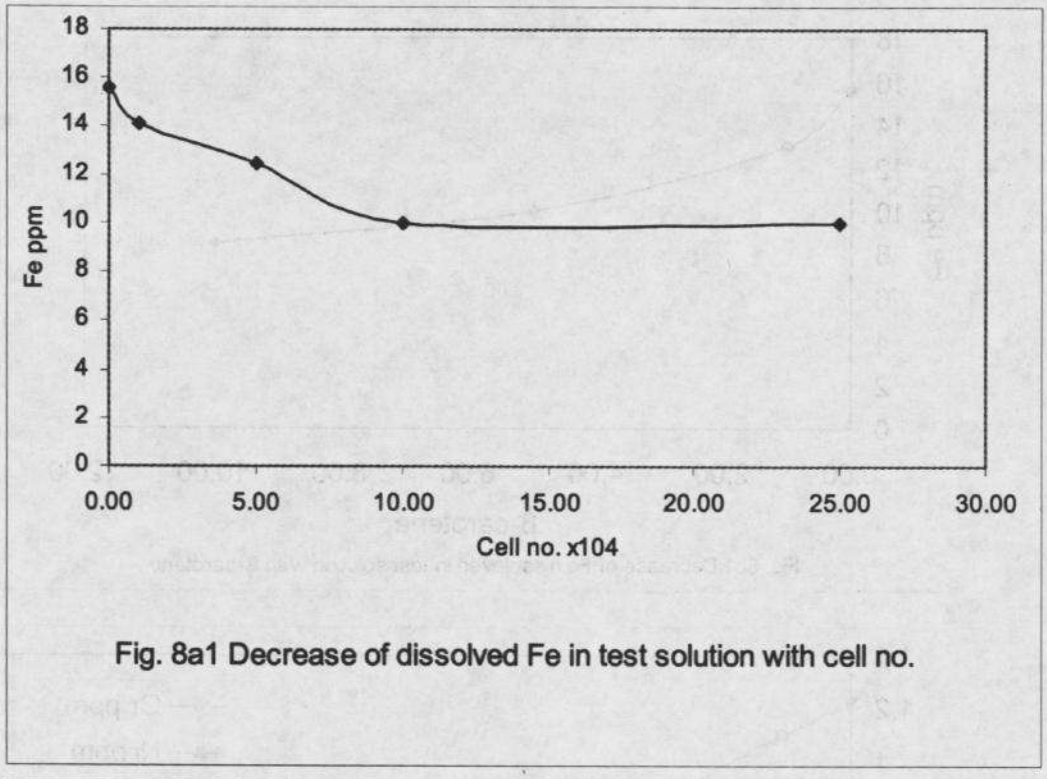

Fig. 8a1 Decrease of dissolved Fe in test solution with cell no.

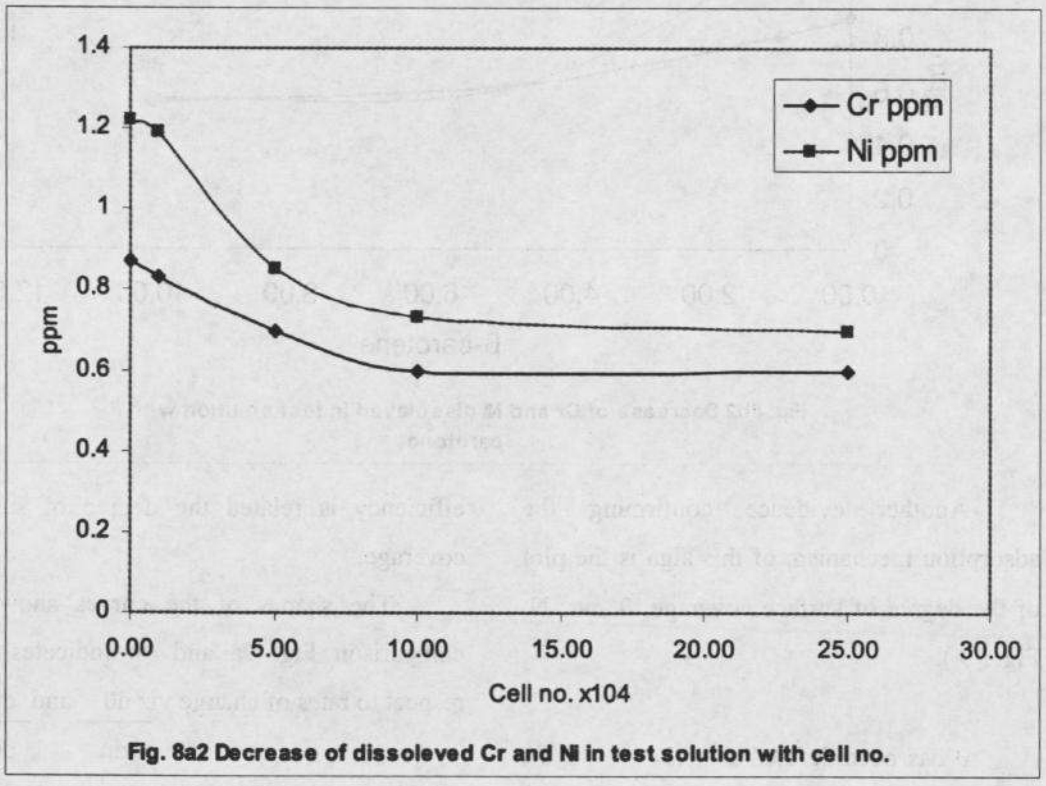

Fig. 8a2 Decrease of dissoleved Cr and Ni in test solution with cell no.

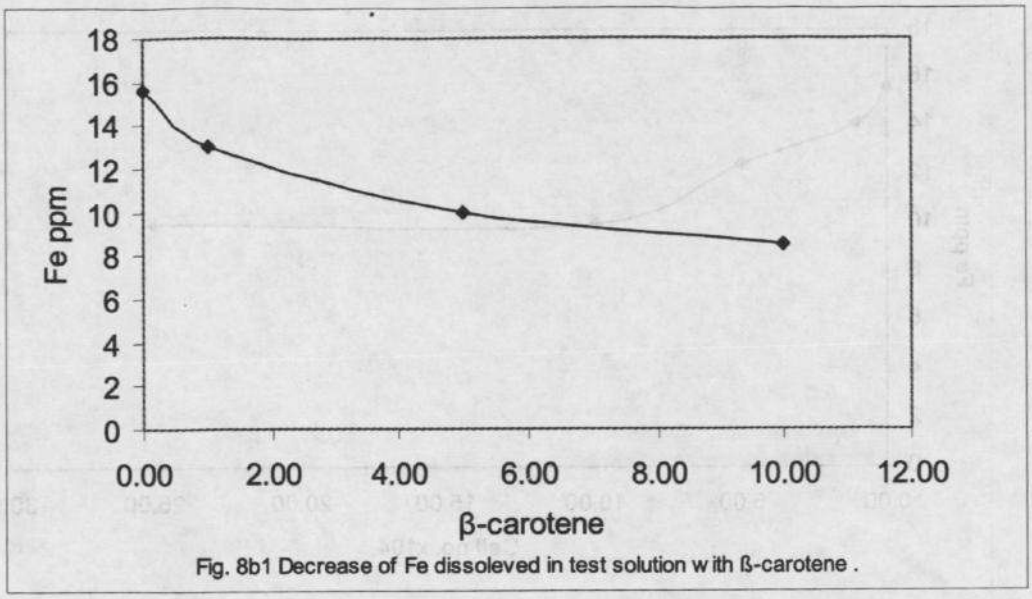

Fig. 8b1 Decrease of Fe dissoleved in test solution with ß-carotene .

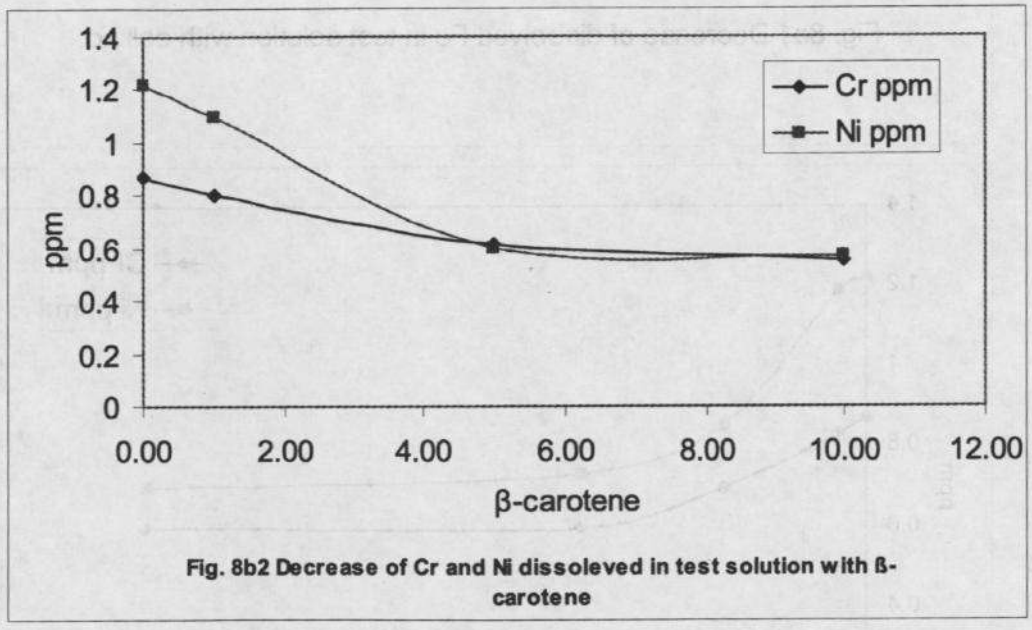

Fig. 8b2 Decrease of Cr and Ni dissoleved in test solution with ß-carotene

Another evidence confirming the adsorption mechanism of this alga is the plot of the degree of surface coverage, θ , vs. N, Fig. (9).

θ has been defined as { (I_0 - I_c) / I_0 }, where I_0 is the corrosion current in the free solution and I_c is the corrosion current in the presence of a given cell number of the alga. The curve in figure (9) is similar to the common adsorption isotherms. Therefore the inhibition efficiency is related the degree of surface coverage.

The shapes of the curves shown in comparison Fig. 9a and 9b indicates with respect to rates of change viz $\frac{d\theta}{dn}$ and $\frac{d\theta}{dc}$ indicate the adsorption of the hole cells is comparable with adsorption isotherm without discussed, where's adsorption of β-caroteneis compare with adsorption isotherm with discusses.

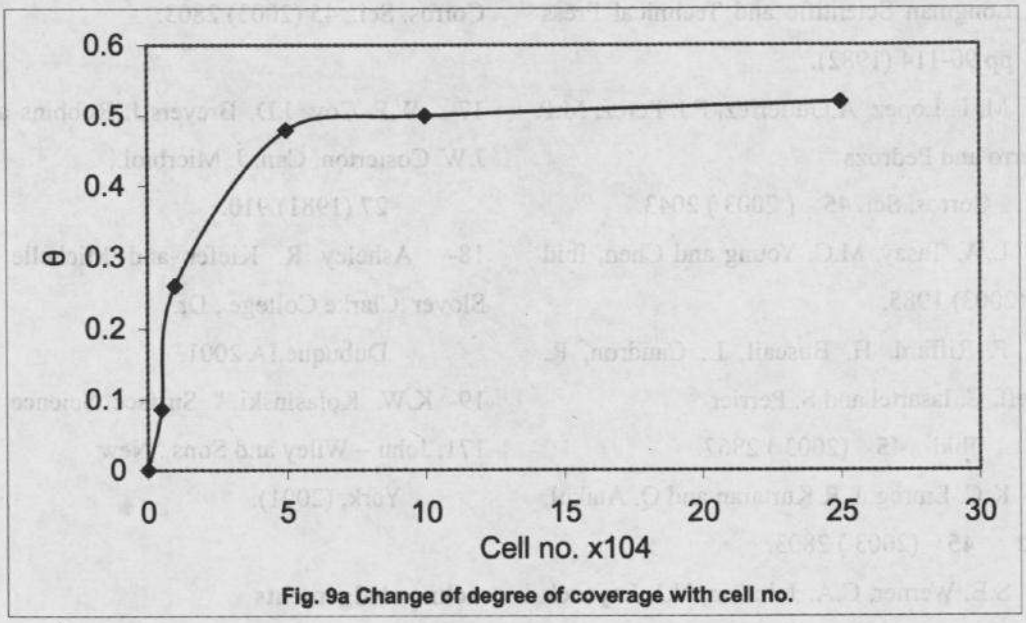

Fig. 9a Change of degree of coverage with cell no.

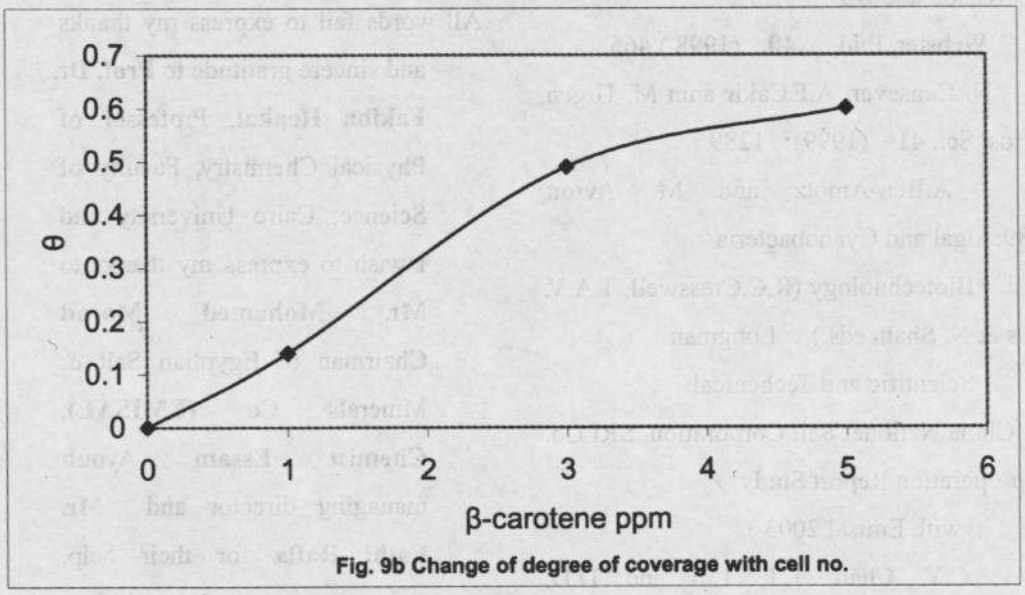

Fig. 9b Change of degree of coverage with cell no.

Conclusion

Corrosion of 304 stainless steel in concentrated saline solutions decreases by 50% in presence of the alga Dunaleilla Salina around its natural abundance. The mechanism of inhibition seem to be the chemisorption of β-carotene secreted from it on the corroding surface.

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