

## Electrochemical Behavior of Titanium Alloy in 3.5% NaCl Containing Natural Product Substances

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Received: 13 March 2011 / Accepted: 24 April 2011 / Published: 1 May 2011

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Marine environment is a complex corrosive system and presence of red algae is one of the factors that influence corrosion processes. Biofouling is one of the major impediments in the use of titanium in sea-water cooled condensers of power plants, which is otherwise an excellent material with respect to corrosion resistance. Electrochemical impedance spectroscopy (EIS) experiments were carried out in 3.5% NaCl to study the corrosion inhibition effect of red algal extracts on Ti-6Al-4V surfaces. The results indicated that the type of extract, the extract concentration and the immersion time affect the inhibition efficiency (IE%). In general, corrosion rate for J1, J2 and J3 [Successive extractions by hexane (J1), ethyl acetate (J2) and methanol (J3)] decreases with increasing its concentration or immersion time. The order of IE% was found to be J3 > J1 > J2. Langmuir adsorption isotherm was found to fit well the experimental data. Values were calculated for the adsorption process and it seemed to be in the order of: J3 (365.66 ppm<sup>-1</sup>) > J1 (150.42 ppm<sup>-1</sup>) > J2 (58.35 ppm<sup>-1</sup>). The results were confirmed by Scanning electron microscope (SEM) photos.

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**Keywords:** EIS, red alga, NaCl, SEM, titanium alloy.

### 1. INTRODUCTION

Traditionally it has been assumed that the interaction of bacteria with metal surfaces always causes increased corrosion rates (microbiologically influenced corrosion MIC). However, more recently it has been observed that many bacteria can reduce corrosion rates of different metals and alloys in many corrosive environments. For example, it has been found that certain strains of *Shewanella* can prevent pitting of Al 2024 in artificial seawater, tarnishing of brass and rusting of mild steel. The mechanism of corrosion protection seems to be different for different bacteria since it has been found that the corrosion potential  $E_{\text{corr}}$  became more negative in the presence of *Shewanella* and algae, but more

positive in the presence of *Bacillus Subtilis* [1]. The term microbiologically influenced corrosion (MIC) is usually interpreted as to indicate an increase in corrosion rates due to the presence of bacteria that accelerate the rates of anodic and/or cathodic corrosion reaction, while leaving the corrosion mechanism more or less unchanged. The possibility of corrosion inhibition caused by microorganisms has rarely been considered [2]. Some researchers have evaluated the concept of corrosion control using regenerative biofilms (CCURB) for a variety of materials such as Al 2024, mild steel and cartridge brass in laboratory tests [3-10]. The chemical and biological activities of the bioactive brominated compounds, nitrogen heterocyclics, nitrogen-sulphur heterocyclics, sterols, terpenoids and sulfated polysaccharides isolated from marine algae, fungi and bacteria have been reviewed [11]. A majority of red algae and almost all the genera of brown algae except *Bodanella*, *Pleurocladia* and *Heribaudiella* occur in salt water. The chemistry of marine natural products has grown normously in the last fifty years. The result is revealed that there is an avalanche of new and biologically exciting marine natural products. However, there is one negative aspect to this work. It is that the isolated compounds are often available in minute amounts. Therefore, if the structure is complex, it is an arduous, and often impossible, task to isolate enough of the natural material for clinical trials.

This is where synthetic chemistry can come to the help of the clinician. Marine natural products are often wonderful challenges to synthetic chemists. The biological activity of an extract of marine organisms or isolated compounds could be assessed in several ways. A fair understanding of biological, toxicological and clinical evaluation is essential to those interested in searching potential drugs from marine organisms. The sulfated polysaccharides obtained from seaweeds are economically the most important products due to their extensive use in food and medicine. Of the four major seaweed classes, the rhodophyceae (red algae), the phaeophyceae (brown algae), the cyanophyceae (blue-green algae) and the chlorophyceae (green algae), the first two classes produce polysaccharides of main interest. The red algae produce carrageenan, agar, agarose, furcellaran or Danish agar. The use of seaweed extracts in food and medicine is reviewed [12]. Marine organisms exhibit a wide range of biological activity [13-15], antioxidant [16], antiviral [17], antibiotic [18], antifungal and antimicrobial activities of marine organisms have been reported [19-24]. The alkaloids are generally defined as naturally occurring basic nitrogenous compounds. Majority of this class of compounds display biological activity.

The reviewers [25-28] of marine alkaloids have, therefore, included amino acids, purines, pyrimidines and their nucleosides, peptides, nitrogenous marine toxins, guanidine etc. under marine alkaloids. In general algae and seaweeds inhabiting different fresh and marine aquatic systems were found to produce different bioactive substances with antimicrobial, antialgal, antiviral, antitumor and anti-inflammatory effects. Algal species belonging to different algal divisions have in addition of their specific pigment contents, different cell wall constituents and produce variable secondary metabolites each has a definite action [29].

Although commercially pure titanium has acceptable mechanical properties and has been used for orthopedic and dental implants, for most applications titanium is alloyed with small amounts of aluminium and vanadium, typically 6% and 4% respectively, by weight. Titanium alloy is used to make propeller shafts and rigging and in the heat exchangers of desalination plants and in heater-chillers for salt water aquariums. Owing to its high stiffness it is favoured in place of steel in high

performance model sailplane. Titanium possesses unique corrosion resistance with protected passive and tenacious oxide film which is generally of  $\text{TiO}_2$  and can have a composite structure which can include  $\text{TiO}$  which is commonly evident in the early stages of formation [30,31]. The corrosion behaviour of Ti-6Al-4V at room temperature has been investigated by a few workers [32,33], the work relating the corrosion behaviour of Ti-6Al-4V with its microstructure and mechanical properties. Historically, Ti alloys have been used in chemical, petrochemical and biomedical applications because of their excellent corrosion resistance and biocompatibility.

The work is concerning to look for biologically active substances from marine red algal extracts against marine corrosive effect on Ti-6Al-4V using EIS technique.

## 2. MATERIALS AND METHODS

Ti-6Al-4V alloy supplied from Johnson and Matthey (England) with composition (wt%); 5.7 Al, 3.85 V, 0.18 Fe, 0.038 C, 0.106 O and 0.035 N and balance titanium. The coupon was welded to an electrical wire and fixed with Araldite epoxy resin in a glass tube leaving cross-sectional area of the specimen  $0.196 \text{ cm}^2$ . The solution used was 3.5% NaCl solution. All reagents are Analar and the solution is prepared using triply distilled water.

The Rhodophyceae (red) seaweed *Jania corniculata* was collected from Mediterranean sea at Alexandria (Abu Quir). The alga was carefully cleaned, washed several times with tap water, distilled water, then air dried away from direct sunlight at room temperature, ground and kept in dark, sterilized, labeled jars till use. Successive extractions by hexane (J1), ethyl acetate (J2) and methanol (J3) were carried out. Filtration of extracts was followed by evaporation of organic solvents at room temperature. The residue of each extract was redissolved by the least volume of the same solvent used for extraction in a preweighed vials, followed by evaporation of solvent and reweighed the extract. Different concentrations (0.016, 0.048, 0.06, 0.07 and 0.08 ppm) were prepared from each extract (J1, J2, J3).

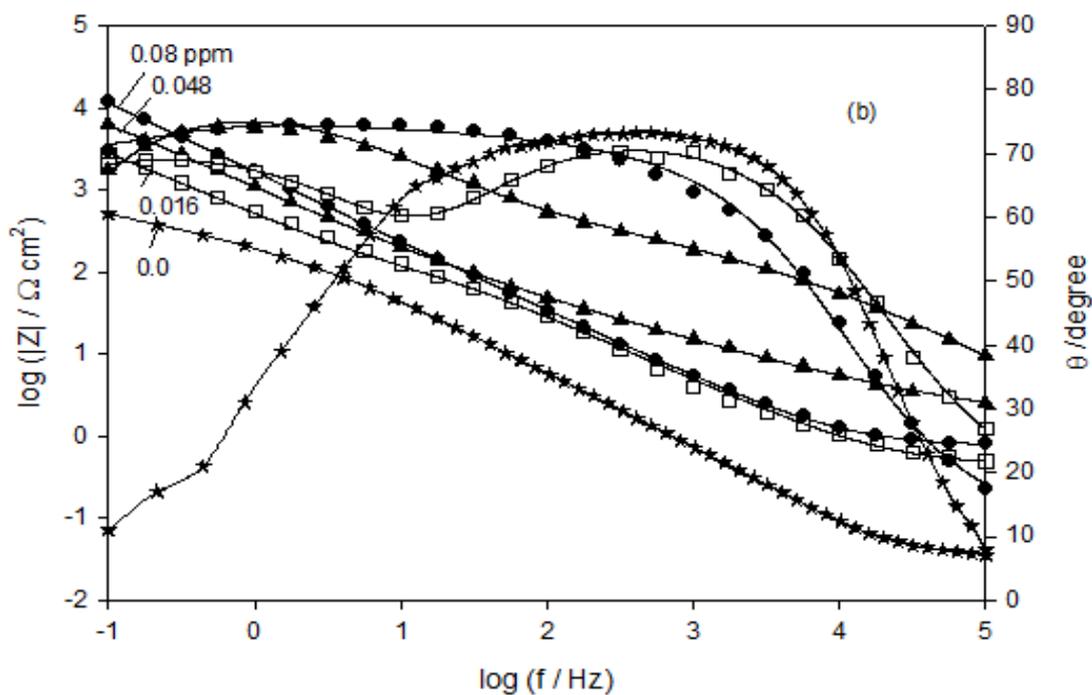
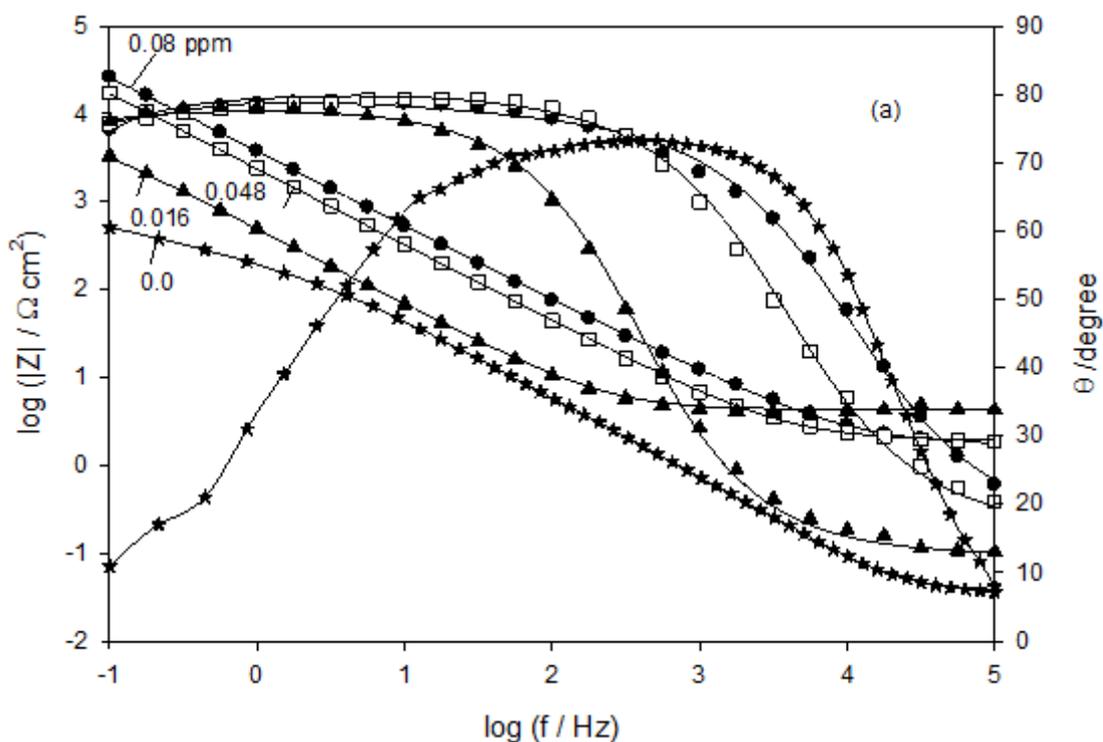
The surface of the test electrode was mechanically polished by emery papers with 400 up to 1000 grit to ensure the same surface roughness, degreasing by acetone, rinsing with ethanol and drying in air. The cell used was a typical three-electrode, one fitted with a large platinum sheet of size 15 x 20 x 2 mm as a counter electrode (CE), saturated calomel (SCE) as a reference electrode (RE) and the alloy as the working electrode (WE).

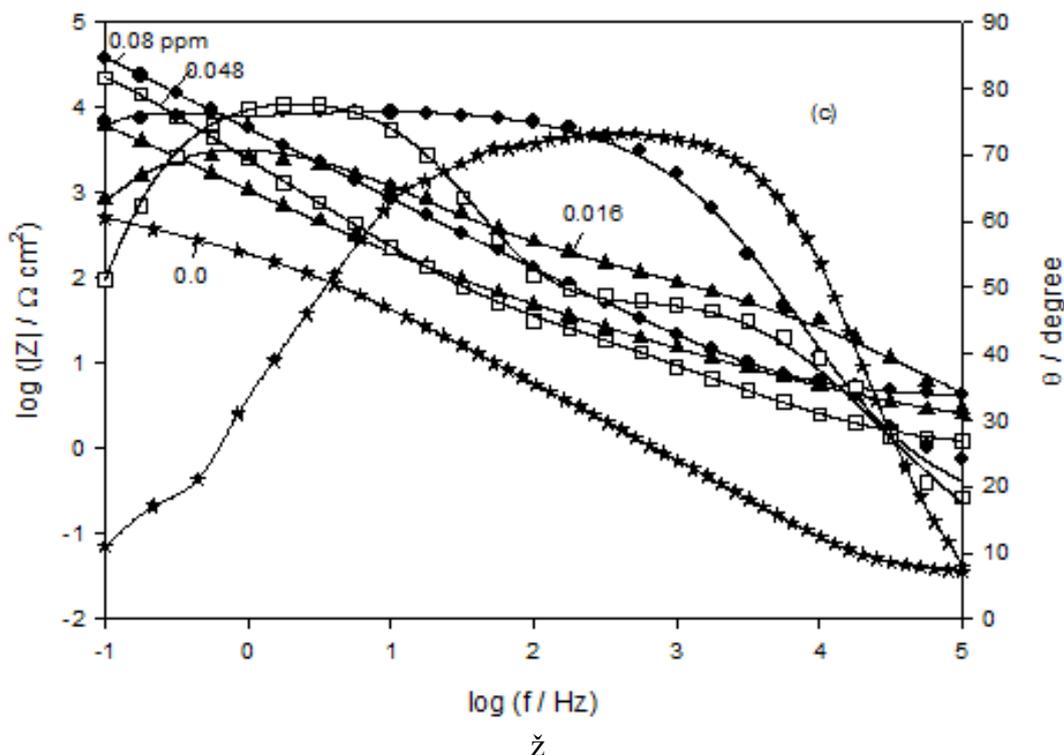
The test solution is 3.5 % NaCl (Analar). The impedance diagrams were recorded at the free immersion potential (OCP) by applying a 10 mV sinusoidal potential through a frequency domain from 10 kHz down to 100 mHz. The instrument used was the electrochemical workstation IM6e Zahner-elektrik, GmbH, (Kronach, Germany). The electrochemical measurements were always carried inside an air thermostat which was kept at 25 °C, unless otherwise stated. All potentials were measured and given with respect to SCE ( $E = 0.241 \text{ V/SHE}$ ). For surface examination, the electron microscope used is JEOL-JEM-100s type with magnification of 50x.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of concentrations of the three *Jania corniculata* extracts

Electrochemical impedance (EIS) is a technique with small perturbative signal and the surface damage of the sample is very little. Besides, the corrosion mechanism can be estimated by analyzing the measured electrochemical impedance spectrum.





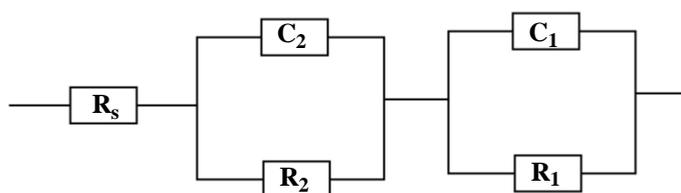
**Figure 1.** (a-c): Bode plots of Ti-6Al-4V alloy in 3.5% NaCl without and with different concentrations of J1, J2 and J3, respectively at 298 K.

In these experiments, Ti-6Al-4V alloy was tested in 3.5% NaCl solution without and with different concentrations of the three *Jania corniculata* extracts: J1, J2 and J3. The EIS scans as Bode plots at different concentrations are given in Fig.1 (a,b,c) for J1, J2 and J3 respectively. It can be seen that these diagrams show resistive regions at high and low frequencies and capacitive contribution at intermediate frequencies. The impedance ( $|Z|$ ) as well as the phase shift  $\theta$  for both alloys is clearly found to depend on both the type and concentrations of three *Jania corniculata* extracts.

**Table 1.** The three *Jania corniculata* extracts (Hexane, ethyl acetate and methanol) exhibited different activities.

Jania	Solvents	The active components
J1	Hexane	Carotenoids Oxygenated carotenoids Fatty acids Sterols
J2	Ethyl acetate	Chlorophyll Di and triterpenoids
J3	Methanol	Phycobiliprotein Phenolic compounds+++ Sulphated polysaccharides Alkaloids

The obtained results, illustrated in Table 1, revealed that the three *Jania corniculata* extracts (Hexane, ethyl acetate and methanol) exhibited different activities. The polar methalonic extract was shown to be the most promising extract inhibiting metal corrosion followed in descending order by hexane (non polar solvent) and finally by the partially polar acetate extract. It has been shown previously that marine macro algae can inhibit the growth of some bacteria [34] and the efficiency of algal extracts against microorganisms is influenced by factors such as location and seasonality [35,36]. Al 2024 is very susceptible to pitting corrosion in seawater; however, it has been found that a number of microorganisms are able to prevent pitting of Al 2024 in AS. These results suggest that microbiologically induced corrosion inhibition (MICI) is a more common phenomenon than was previously assumed. It has been shown that MICI occurs only in the presence of a live biofilm [10]. This may be due to the synergetic effect of the compounds of J3 are antioxidant and have the ability to scavenge any free radicals present at the surface and decrease the corrosion. J1 also have antioxidant compounds but less than J3 while J2 has the lowest one as shown in Table1.



**Figure 2.** Equivalent circuit model representing two time constants for an electrode/electrolyte solution interface.

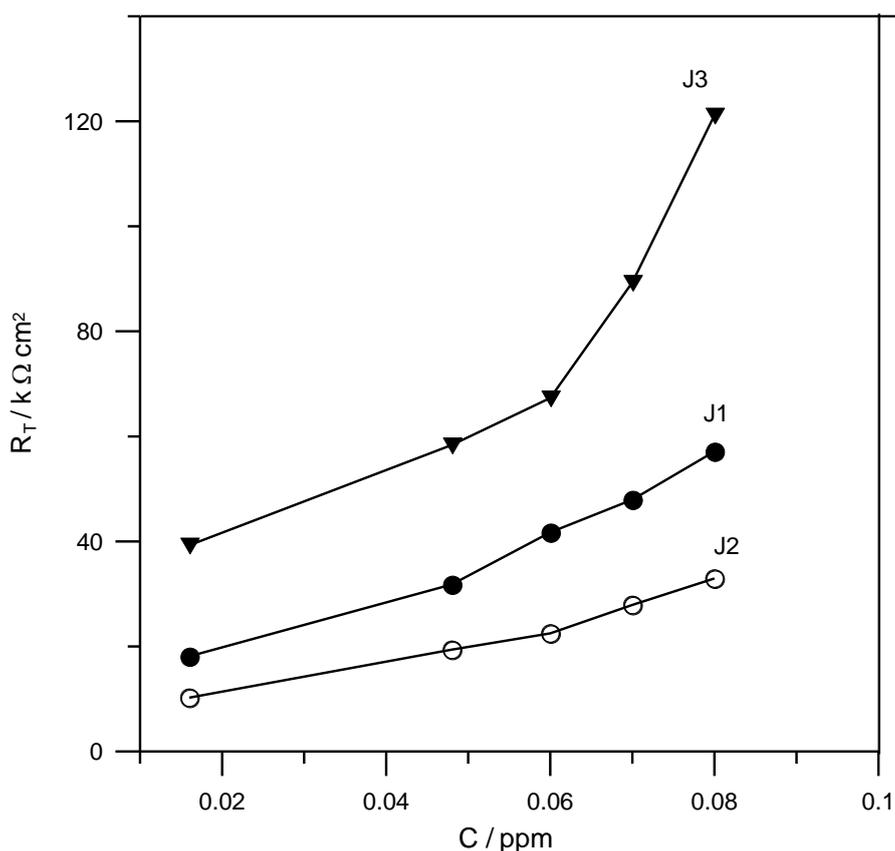
The Bode format of Fig. 1 confirms the presence of two time constants as there are two maximum phase lags appears at medium frequencies (MF), and low frequencies (LF). On the other hand, for the impedance diagrams with two time constants the appropriate equivalent model, shown in Fig. 2, consists of two circuits in series from  $R_1C_1$  and  $R_2C_2$  parallel combination and the two are in series with  $R_s$ . In this way  $C_1$  is related to contribution from the capacitance of the outer layer and the faradaic reaction therein and  $C_2$  pertains to the inner layer, while  $R_1$  and  $R_2$  are the respective resistances of the outer and inner layers constituting the surface film, respectively [37,38]. Analysis of the experimental spectra was made by best fitting to the corresponding equivalent circuit using Thales software provided with the workstation where the dispersion formula suitable to each model was used [39]. In this complex formula an empirical exponent ( $\alpha$ ) varying between 0 and 1, is introduced to account for the deviation from the ideal capacitive behavior due to surface inhomogeneties, roughness factors and adsorption effects [40]. In all cases, good conformity between theoretical and experimental was obtained for the whole frequency range with an average error of 3%. For this model the electrode impedance is represented by the following transfer function [41]:

$$Z(\omega) = R_o + \frac{R_1}{1 + R_1C_1(j\omega)^{\alpha_1}} + \frac{R_2}{1 + R_2C_2(j\omega)^{\alpha_2}} \tag{1}$$

The above formula takes into account the deviation from the ideal RC behavior and considers, for a more realistic approach that each oxide layer as non-homogeneous. Thereby, the impedance associated with the capacitance of each layer is described by a constant phase element (CPE). By this way  $C_1$  is related to contributions from the capacitance of the porous (outer) layer and  $C_2$  of the barrier inner layer while  $R_1$  is the resistance of the outer porous layer and  $R_2$  of the barrier layer [42]. For this model, the total reciprocal capacitance is given by the well-known relation:

$$C_T^{-1} = C_1^{-1} + C_2^{-1} \quad (2)$$

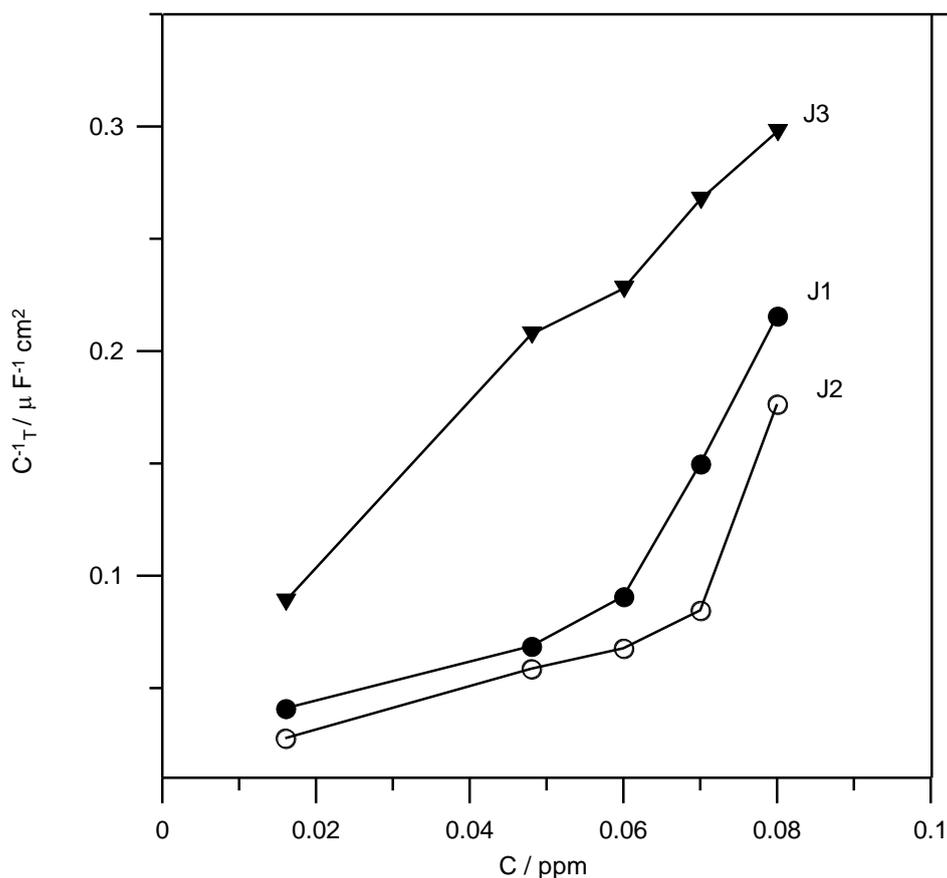
The estimated theoretical impedance parameters are collected in Table 2 for the tested solutions of various concentrations.



**Figure 3.** Dependence of  $R_T$  on the Jania concentrations for Ti-6Al-4V alloys in 3.5% NaCl containing J1, J2 and J3 at 298 K.

Figs. 3 and 4 display the total resistance ( $R_T = R_1 + R_2$ ) and  $C_T^{-1}$  of the surface film as a function of the Jania concentration, respectively. The results indicate that both  $R_T$  and  $C_T^{-1}$  increase rapidly with the increase of Jania concentration, and also their values depend on the type of extract. In general the values of  $C_T^{-1}$  and  $R_T$  are in the order of:  $J3 > J1 > J2$ . This result could be due to the formation of

inhibiting species by the biofilm as suggested by Eashwar et al [43] or to a reduction of the chloride concentration at the surface that is covered by the biofilm.

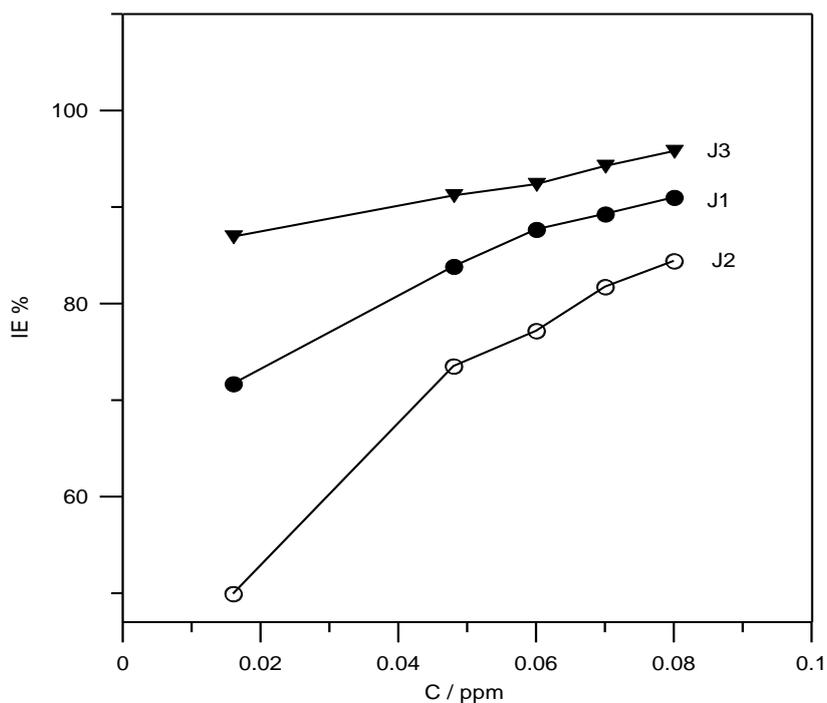


**Figure 4.** Dependence of  $C_T^{-1}$  on the Jania concentrations for Ti-6Al-4V alloys in 3.5% NaCl containing J1, J2 and J3 at 298 K.

They observed that the impedance for these two materials did not change with time despite formation of a biofilm and suggested that the porous and water-like structure of the biofilm did not produce the characteristic changes in the impedance spectra that result from the application of protective polymer coatings [44]. As also discussed [45], the decrease of the corrosion rate of mild steel in the presence of *Shewanella* is due to a reduction of the rate of both the anodic and the cathodic reaction. The fairly high values of  $R_T$ , which approached to 122.15 kΩ cm<sup>2</sup> range for J3 at 0.080 ppm, suggest that pits formed in the initial stages of exposure have become passivated. Very similar results were obtained in the presence of *B. subtilis* producing polyglutamate or polyaspartate [3-6]. The increased  $R_T$  values suggest that the inhibitors produced by Jania provided additional corrosion protection suggesting that corrosion inhibition is due mainly to a decrease of the rate of oxygen reduction at the metal surface [10].

**Table 2.** Impedance parameters for Ti-6Al-4V alloy as a function of concentration in 3.5% NaCl containing Jania at 298 K.

Jania	Conc. ppm	$R_s / \Omega \text{ cm}^2$	$R_1 / \text{k}\Omega \text{ cm}^2$	$C_1 / \mu\text{F cm}^{-2}$	$\alpha_1$	$R_2 / \text{k}\Omega \text{ cm}^2$	$C_2 / \mu\text{F cm}^{-2}$	$\alpha_2$
Blank	0.00	0.06	5.12	112.3	0.89	0.01	133.41	0.79
J1	0.016	4.25	16.79	43.32	0.95	1.31	55.95	0.86
	0.048	1.84	30.11	25.82	0.96	1.69	33.42	0.85
	0.060	1.83	40.01	17.72	0.97	1.71	29.11	0.86
	0.070	1.83	45.98	9.10	0.98	1.98	25.00	0.85
	0.080	1.85	55.07	6.11	0.96	2.06	19.10	0.91
J2	0.016	0.91	10.14	84.17	0.88	0.11	63.45	0.83
	0.048	1.94	19.20	29.00	0.91	0.18	41.52	0.85
	0.060	1.98	22.30	25.00	0.94	0.19	36.11	0.90
	0.070	1.89	27.89	20.01	0.96	0.22	28.93	0.91
	0.080	1.68	32.67	17.43	0.97	0.27	8.42	0.93
J3	0.016	0.97	36.46	18.36	0.99	2.82	29.29	0.91
	0.048	1.67	51.74	6.62	0.98	6.61	17.64	0.88
	0.060	3.56	60.20	5.96	0.98	7.11	16.66	0.90
	0.070	4.10	80.45	5.03	0.99	8.87	14.58	0.92
	0.080	4.21	110.35	4.59	0.98	11.80	12.52	0.91

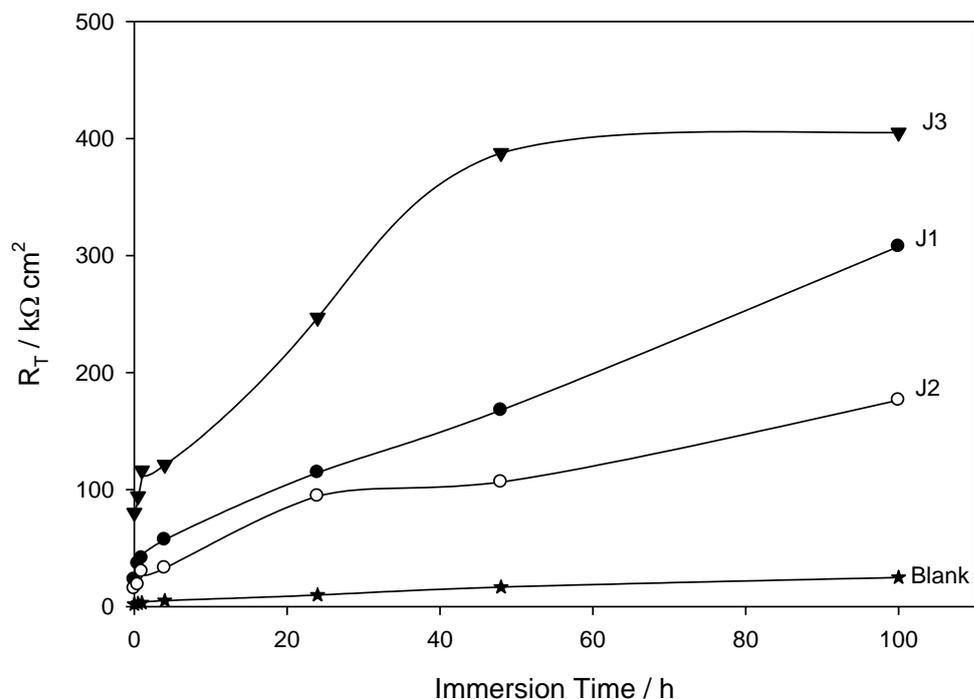


**Figure 5.** The relation between the inhibition efficiency and the concentration of J1, J2 and J3 in 3.5% NaCl .

The experimental values are correlated to the theoretical impedance parameters of the equivalent model and listed in Table 2. As given in Table 2, it was found that film healing and thickening ( $C_T^{-1}$ ) becomes effective by increasing the concentrations of the three extracted jania. This is caused by the formation of adherent corrosion products on the sample surface. As shown in Fig.5, the inhibition efficiency increases with Jania concentration and also it is higher for J3 then J1 and J2 which has the lowest one. At 0.080 ppm it reaches 97% for J3, 90% for J1 and 83% for J2. Such action could be explained through that the polar extract of red alga *Jania Coniculata* (J3) contains the pigments characteristic of the red algae which is the phycobiliproteins(which include phycocyanin and phycoerythrin) together with the sulphated polysaccharides, as well as large proportions of phenolic compounds and alkaloids. Each of these compounds in the polar extract may have its own inhibitory activity of metal corrosion. Also they may act synergistically leading to large detectable increase in protection against corrosion.

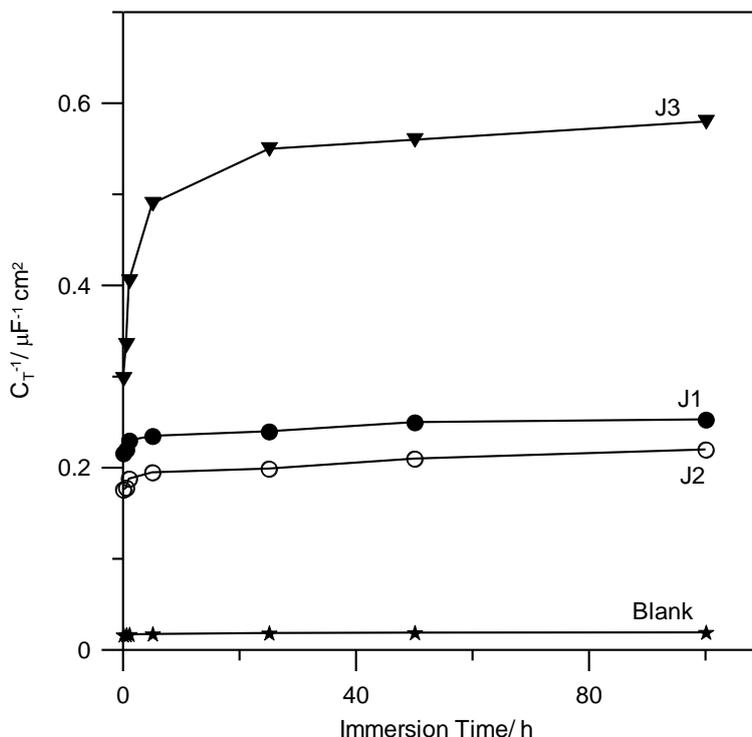
### 3.2. Effect of immersion time

EIS is a useful technique for long time tests, because they don't significantly disturb the system and it is possible to follow it over time [46].



**Figure 6.** Dependence of  $R_T$  on the immersion time for Ti-6Al-4V alloys in 3.5 % NaCl without and with 0.080 ppm of J1, J2 and J3 at 298 K.

The present work was carried out in 3.5% NaCl containing 0.080 ppm of J1, J2 or J3 for 100 hours immersion time. From EIS data, it is obvious that both  $R_T$  and  $C_T^{-1}$  values increased sharply with immersion time as shown in Figs. 6 & 7, respectively. The formation of the inhibitor surface film, and therefore the inhibitor adsorption, on the electrode surface was fast and completed within 50 h for J3. This is consistent with the synergistic effect of inhibitor (due to adsorption) and Ti alloy corrosion products to increase the protective power of the passive film and a compact adsorbed film of the inhibitor is formed on the surface.



**Figure 7.** Dependence of  $C_T^{-1}$  on the immersion time for Ti-6Al-4V alloys in 3.5 % NaCl without and with 0.080 ppm of J1, J2 and J3 at 298 K.

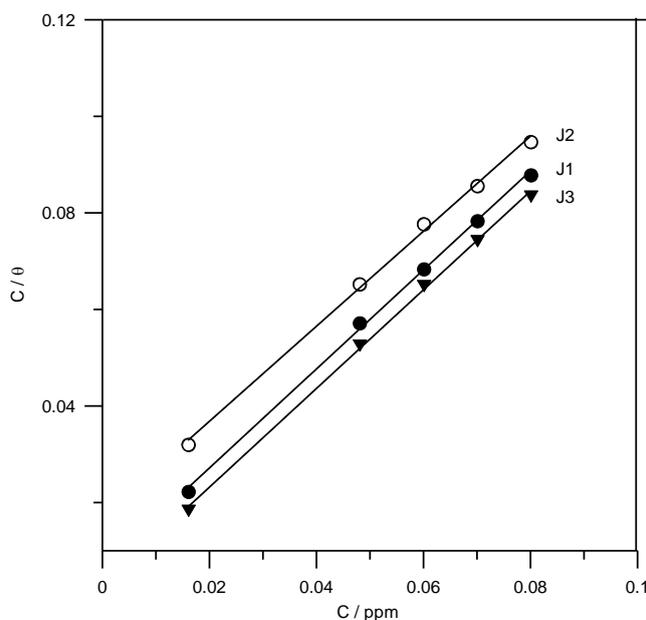
### 3.3. Adsorption isotherms

With regard to Langmuir adsorption isotherm, Eq. (3), it was found to fit well with the experimental data obtained. Where  $\theta$  is the surface coverage (IE %) / 100 of the inhibitor on the Titanium alloy surface which is related to the concentration (C) of the inhibitor in the bulk of solution according to the following equation:

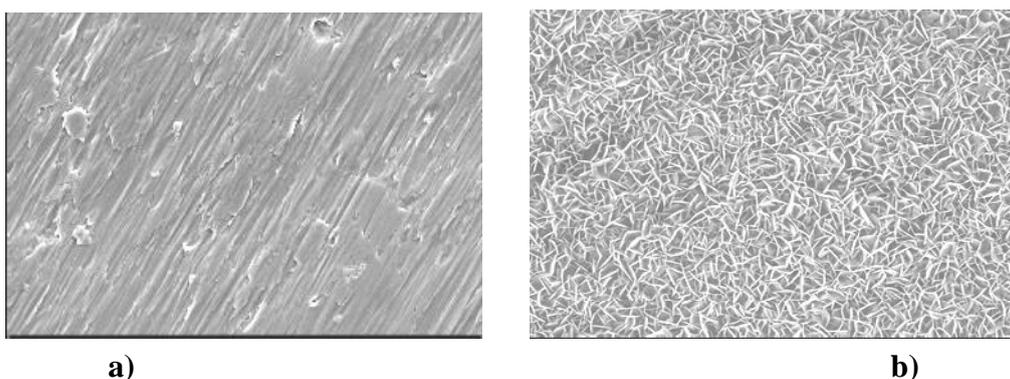
$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{3}$$

$K_{ads}$  is the adsorption-desorption equilibrium constant. By plotting  $C/\theta$  versus  $C$  at 298K for the three inhibitors, straight lines were obtained as seen in Fig.8. From the intercepts,  $K_{ads}$  values were calculated for the adsorption process. The equilibrium constant of adsorption is seen to be in the order of: J3 ( $365.66 \text{ ppm}^{-1}$ ) > J1 ( $150.42 \text{ ppm}^{-1}$ ) > J2 ( $58.35 \text{ ppm}^{-1}$ ). The  $K_{ads}$  values may be taken as a measure of the strength of the adsorption forces between the inhibitor molecules and the metal surface [47]. Therefore, the strongest interaction between the double layer existing at the phase boundary and the adsorbed molecules and the highest IE% are owing to J3.

The surface morphology of Ti alloy was studied by scanning electron microscopy (SEM). Fig. 9(a,b) shows the SEM photograph of Ti-6Al-4V surface without and with 0.080 ppm of J3 after 50 h in 3.5% NaCl. The SEM photographs showed that the surface of metal has corrosion product(a), but in presence of inhibitor(J3) they are minimized on the metal surface(b). It indicates the formation of passive layer on the metal surface. So the corrosion rate is decreased in the presence of Jania (polar extract).



**Figure 8.** Langmuir adsorption isotherm of J1, J2 and J3 on Ti-6Al-4V surface.



**Figure 9.** SEM micrographs for Ti-6Al-4V alloy after 50 h of immersion in 3.5% NaCl: (a) without J3 (b) with 0.80 ppm of J3.

#### 4. CONCLUSIONS

- The corrosion inhibition of titanium alloy increases in presence of three different red algal extracts in 3.5% NaCl solution.
- The corrosion inhibition in 3.5% NaCl is in the order of: J3 > J1 > J2.
- The total resistance  $R_T$  and the relative thickness  $C_T^{-1}$  of the film formed on titanium alloy in 3.5% NaCl is in the order of : J3 > J1 > J2.
- The corrosion of titanium alloy in 3.5% NaCl can be effectively inhibited by addition of Jania extract and increasing with concentration, this was confirmed by SEM images.

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