Research Article

Novel Corrosion Inhibitors Based On Seaweeds for AA7075 Aircraft Aluminium Alloys

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Abstract
Sodium alginate was extracted from brown seaweed species of Turbinaria and Sargasum. Corrosion studies were carried out on AA 7075 aluminium alloys using the sodium alginate extracted from Turbinaria ornata. The functional groups in the seaweed and the extracted alginate were studied using ATR-IR spectroscopy and the presences of suitable functional groups were confirmed. The AA7075 samples coated with 2000ppm Sodium Alginate inhibitor showed improve corrosion inhibition. A maximum efficiency of 95% was observed for a 24 hour immersion in 3.5% NaCl solution which was used as the corrosive media.

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Introduction

Hexavalent Chromium (Cr^{6+}) compounds are being used in aviation industry for almost 8 decades to combat corrosion of aircraft aluminum components. These compounds are generally used in hard chrome plating, chromic acid anodizing (CAA) and chromate conversion coatings (CCC) as well as corrosion inhibitors in primer formulations owing to their superior corrosion protection of aircraft aluminum components. CCCs and CAA are used as primary treatment to not only to provide better adhesion to the next primer layer but also provides excellent cathodic and anodic corrosion inhibition properties to the metals. In primary treatment these Cr^{6+} compounds are trapped into the chromium oxide/hydroxide film, whereas in epoxy primer formulations chromates are added as inhibitors (e.g. Strontium Chromate, Lead Chromate, etc.) to heal the damage caused by the corrosive ion attack over the metal surface. The mechanism involved in the corrosion mitigation of Hexavalent chromium is well established and generally involves in two stages. (i) The Cr^{6+} in the form of CrO_4^{2-} / $Cr_2O_7^{2-}$/ $Cr_3O_{10}^{2-}$ is soluble and hence easily dissolves in the aqueous corrosive medium and migrates to the affected sites and (ii) formation of insoluble Chromium (III) oxides [1].

Today, aircraft companies across the world are striving towards complete removal of chromates. The reason evolving the "complete" removal of chromates is the high level of toxicity and health hazards associated with it. Cr^{6+} compounds are considered to be occupational carcinogens by various regulatory organizations viz. Occupational Safety and Health Administration (OSHA-USA), National Institute of Occupational Safety and Health (NIOSH-USA), Environmental Protection Agency (EPA-USA), European Agency for Safety and Health at Work (EU-OSHA), etc. $Cr^{6+}$is associated with lung, nasal and sinus cancer. At still higher concentrations, it could affect the genes too, thus classified as a genotoxic carcinogen. In aircraft painting, workers are often exposed to high concentration of airborne hexavalent chromium. According to OSHA, there are 5,58,000 workers exposed to Cr^{6+} [2-4]. Apart from the direct occupational hazard associated with hexavalent chromium, people get affected through the Cr^{6+}polluted water resources.

There is no universal replacement for chromates in the industry, due to the unique and excellent mechanism of chromates in protecting the aluminum components from corrosion. The most vital barrier in finding the effective replacements are in replicating the self-healing property of chromates. The ultimate possible non-toxic replacement could be procured from the nature itself. Recently, Dr. Husnu Gerenji have found that the juice from dates palm could inhibit the corrosion of AA 7075 alloy widely used in aerospace and defense applications[5]. The use of a date's fruit juice for an industrial application greatly raises the question of endangering food chain and also the medicinal values associated with it. The exploitation of land based plants for industrial applications will highly affect the fresh water ecosystem, food chain and medicinal values. Brown seaweeds such as Laminaria are exploited and farmed for their alginate value, which is used as a gelling agent in food, wound dressings, biomedical applications and as a template for nanoparticles synthesis, to name a few. Alginate is a bio-polysaccharide comprising of β-D mannuronic acid and α-L guluronic acid units[6]. Seaweed species like Turbinaria and Sargassum doesn't find much applications in food processing, yet contain high amount of alginate (around 60 wt. %) which have been utilized for our corrosion inhibition application.

Experimental Procedure

The brown seaweeds of species Turbinaria was collected from Kilakarai Coast, a southern district in Tamil Nadu, India. The collected weeds were shade dried for around 4 days and washed well with tap water and deionized water to remove the epiphytes and salts from the seaweeds. The washed seaweeds were then subjected to air-drying at 60 ^{0}C for 2 hours. It was then ground to fine powders using pestle and mortar. The extraction of alginate was performed by the alkaline extract route. The powders were immersed in 0.1 M H_2SO_4 solution overnight. It was then subjected to 2 wt. % Na_2CO_3 treatment with mild stirring for 24 h at 60-65 ^{0}C. The formed viscous solution was filtered using muslin cloth with excess water. The water soluble alginate was precipitated using ethanol. The precipitated product was filtered and dried in air oven at 65^{0}C to get the final product. The yield of the alginate was measured as the weight percentage. The yield of alginate from the Turbinaria was found to be around 58%. The yield value presented is purely based on our experiment. It may differ with various other environmental conditions. The functional groups present in the seaweed and the extracted alginate was analyzed using ATR-IR spectroscopy in the reflection mode using Perkin Elmer-spectrum two spectrophotometer in the range of 400 to 4000 cm^{-1}. The aluminum alloy AA 7075 sheets of thickness 1.5 mm were cut to the size of 20 mm*15 mm for the experimental usage. The cut samples were subjected to polishing using SiC papers of grit sizes 200, 600, 800 and were subjected to polishing using Alumina powders of 1μ size. The samples were tested for their corrosion resistance in 3.5% NaCl solution. Sodium Alginate extracted from brown seaweed Turbinaria ornata was used as the corrosion inhibitor. Initially, the concentration of inhibitors tested was 500, 1000, 1500 and 2000 ppm. The material tested with 2000 ppm was found to have optimized level of inhibition compared to the others. Hence, further experiments were carried out with 2000 ppm of inhibitor compound. The aluminum alloy samples were tested for its initial corrosion resistance in the corrosive media with and without adding the inhibitor. For further testing of inhibition efficiency, the samples were immersed in the media in the presence and absence of 2000 ppm of sodium alginate for the period of 24, 72, 120 and 240 h. The Corrosion resistance was measured by Potentiodynamic polarization experiment.

The test setup that was used is the conventional three-electrode system with substrate as working electrode (WE), Pt and saturated calomel electrode (SCE) as counter (CE) and reference (RE) electrodes respectively. Potentiodynamic polarization studies were carried out in the range of OCP±0.25V with the scan rate of 0.001 V/s. The potentiodynamic polarization results are represented as potential vs. log i plot.

Results and Discussions

a) ATR – IR Results

Figure 2 shows the ATR – IR spectra of the seaweed Turbinaria ornata and the extracted sodium alginate solution. For the seaweed Turbinaria ornata, the bands around 800 cm-1 corresponds to the C-H "out of plane" of the aromatic ring. The strong transmittance near 1040 cm-1 is due to the stretching vibrations of C-O bond. The presence of aliphatic amine is confirmed by the transmittance near 1230 and 1600 cm^{-1}, which correspond to C-N stretching and N-H bending vibrations respectively. The strong band around 3400 cm-1 is due to the O-H stretching vibrations in the alcoholic groups. C=O stretching vibrations due to the carboxylic acids group is also present. The alginate extracted from Turbinaria ornata also shows similar trend in the bands due to the O-H, C-H, COOH and C-O vibrations, which further confirms the alginate functional groups.

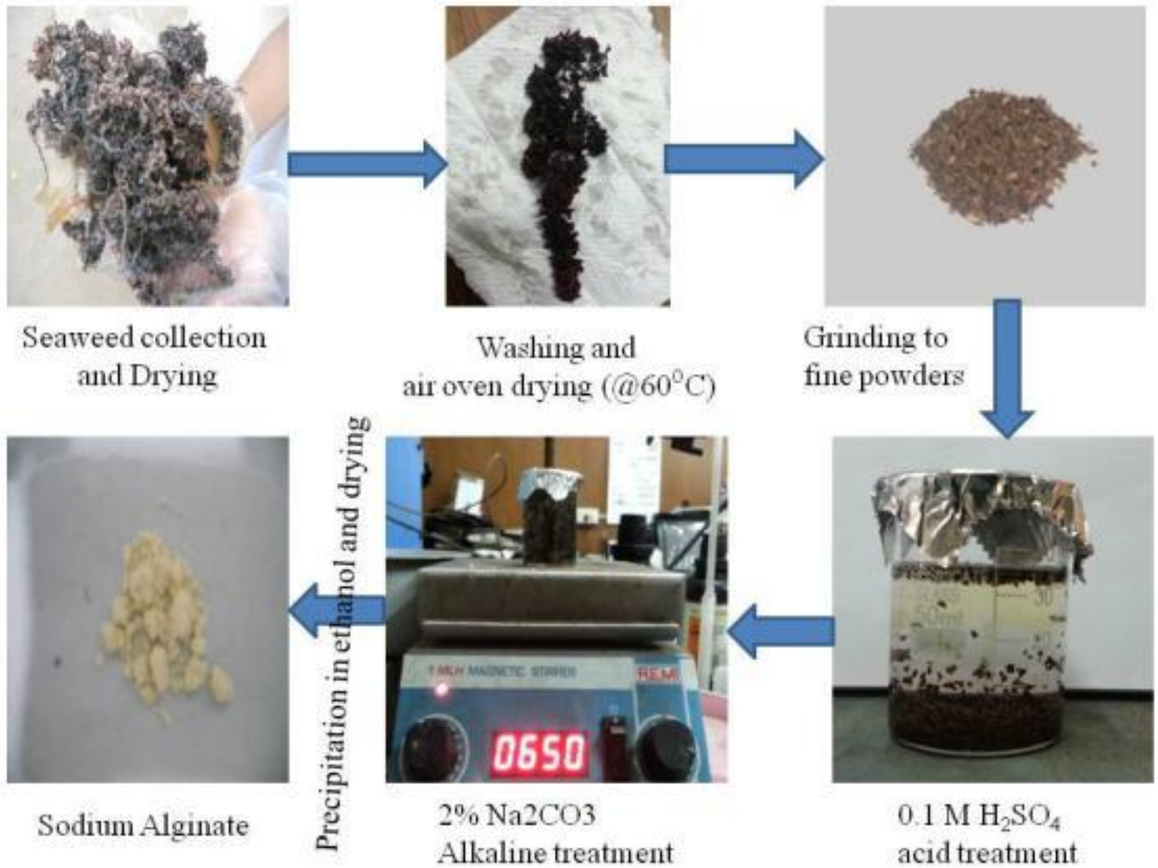

Figure 1 Alkaline Extraction Process of Sodium Alginate from Turbinaria ornata

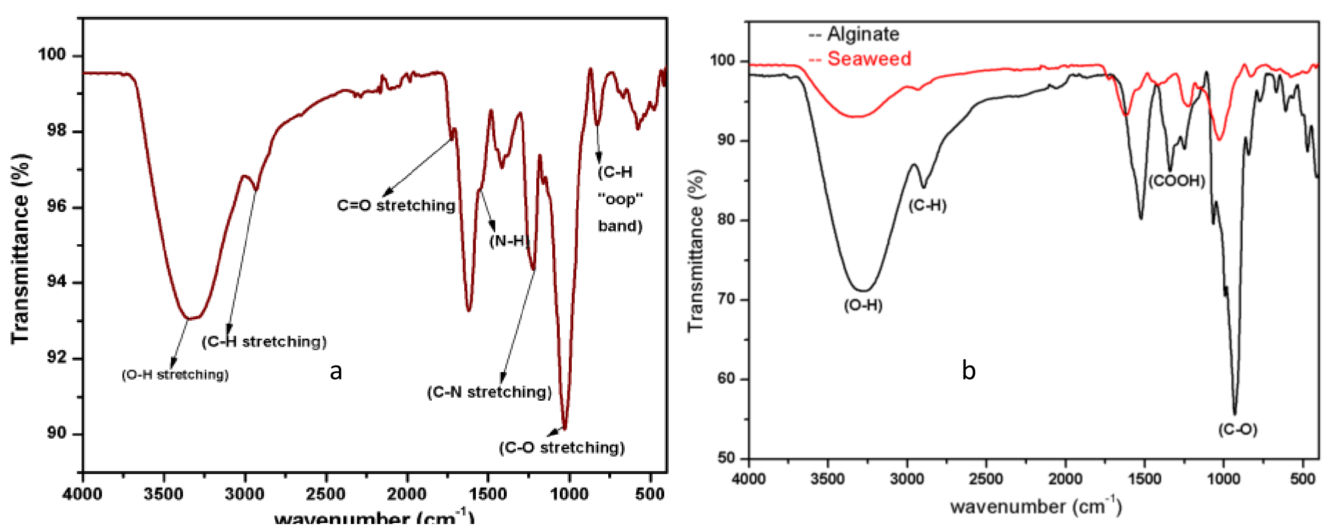

Figure 2 ATR-IR spectra of Turbinaria ornata seaweed (a) and extracted alginate (b) used for experiment

Corrosion Studies

From the following figures (Figure 3 and 4), it can be seen that the i_{corr} values of aluminum alloy samples immersed in inhibitor containing medium was found to be very much lower than that of the samples immersed in the solution containing no inhibitor. This variation shows that the corrosion resistance of the aluminum alloy AA 7075 increases drastically with the addition of sodium alginate as inhibiting compound. The inhibition efficiency was calculated for each case which is tabulated in Table 1. This inhibiting effect may be due to the formation of stable aluminum alginate complex film over the alloy surface, which resists the further corrosive attack.

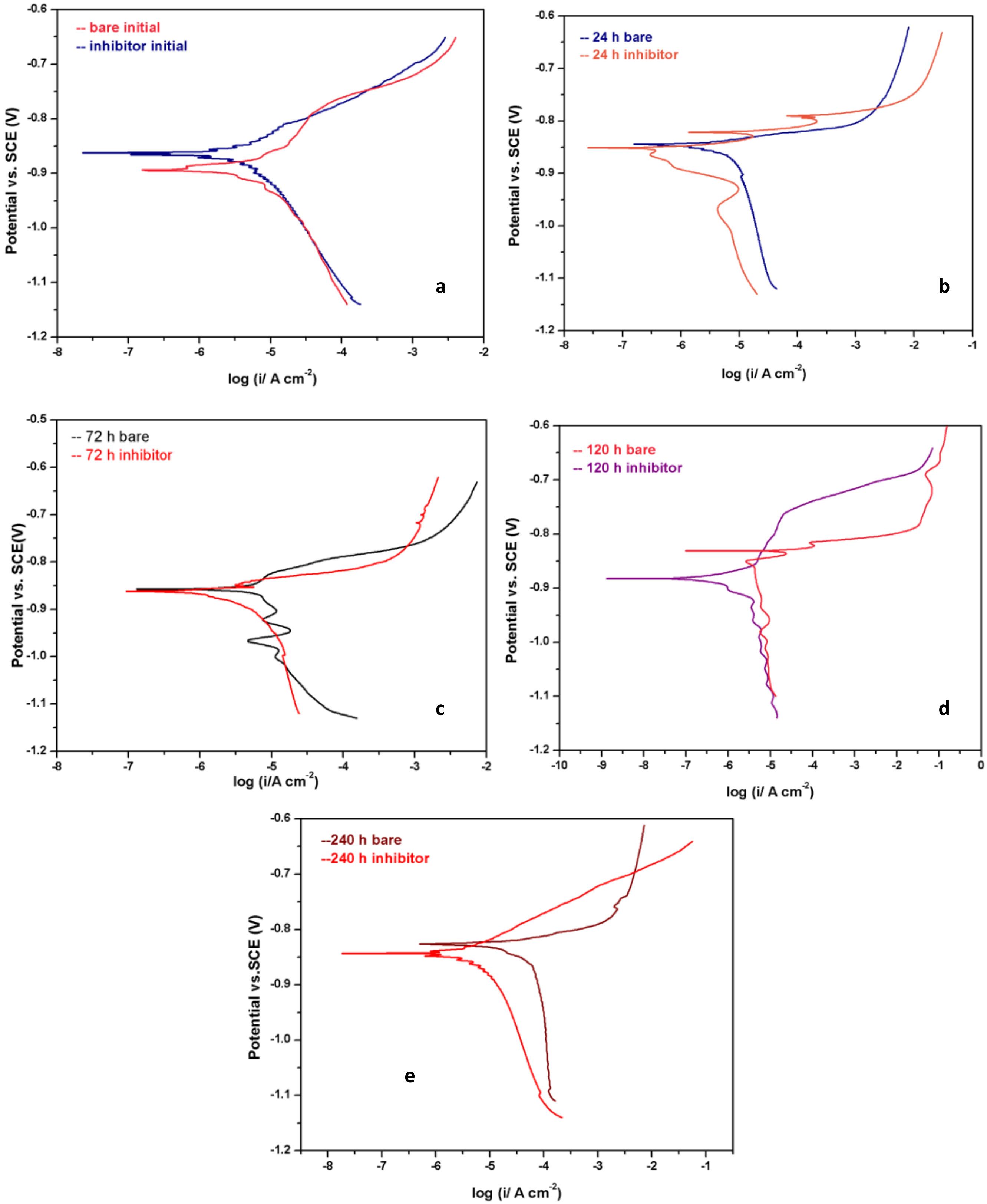

Figure 3 Potentiodynamic polarization curves of (a) Initial Sample and samples after (b) 24h (c) 72h (d) 120h and (e) 240h of immersion in 3.5% NaCl solution in presence of inhibitor (2000ppm) and absence of inhibitor.

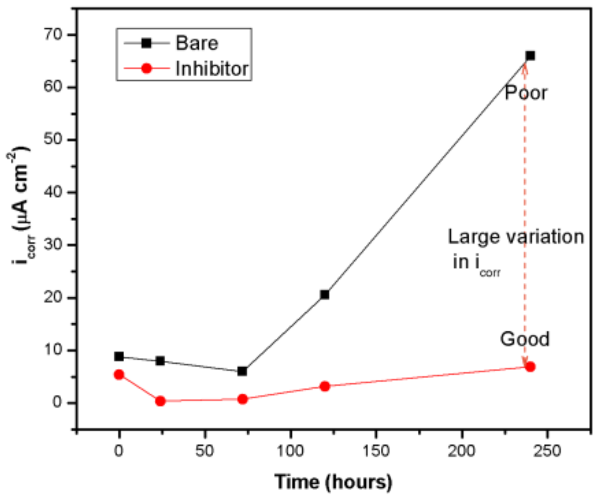

Figure 4 Variation of i_{corr} with immersion duration

Table 1 Inhibition Efficiency with Immersion duration

Immersion Time (hours)	i_{corr} (bare) (μA cm^{-2})	i_{corr} (inhibitor) (μA cm^{-2})	Inhibition Efficiency (%)
Initial	8.7962	5.4200	---
24	7.3977	0.3604	95.13
72	5.9700	0.7073	88.15
120	20.525	3.1196	84.80
240	65.996	6.8800	89.57

The maximum inhibition efficiency achieved was ~ 95% for 24 hrs duration of immersion in the media and the average efficiency achieved over the 240 hours of immersion study is around 89% (89.4125%).
Alginates have the property of cross-linking with the divalent and polyvalent metal ions in the solution to form stable complexes[6], which is the basis of our study. Sodium alginate, which is soluble in aqueous solution, moves towards the sites of localized corrosion, reacts with the aluminum ions (Al^{3+}) present on the surface, and cross-links to form corrosion inhibiting, insoluble and stable Aluminum-Alginate complex film. Theoretically, this could be the possible mechanism of corrosion inhibition of aluminum by sodium alginate, an aqueous extract from brown seaweeds in seawater environment.

Conclusion

Sodium alginate was extracted from the seaweed Turbinaria ornata and the yield of the alginate obtained was around 58%. ATR – IR results of the extract showed the presence of O-H, C-H, COOH and C-O vibrations, which confirmed the alginate functional groups in the extract. A solution with 2000ppm of the alginate was used as the inhibitor for the AA7075 aluminium alloys. After a period of 24 hour immersion in the 3.5% NaCl, the specimen with the inhibitor showed an increase in efficiency by 95.13% in comparison with the absence of the inhibitor compound. Thus, the alginates that were investigated in the present research could be suitable replacements for the chromium based inhibitors used in aircrafts today.

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