

The benefits of *k*-Carrageenan-gelatin hybrid composite coating on the medical grade stainless steel (SS304) used as anticorrosive barrier

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Abstract

Biopolymers derived from seaweed are good anticorrosive, antibacterial and anticancer agents. These biopolymers family includes the *k*-Carrageenan with good potential anticorrosive feature that is extracted from the red seaweed *Acanthophora spicifera* - *Rhodophyceae*. To obtain the best corrosion inhibition properties the *k* -Carrageenan hybrid composite with gelatin was prepared by sol-gel method. In the present study, two natural compounds have been used to prepare the proposed hybrid composite material. Such as, a self-assembled multilayer coating for medical grade stainless steel (SS) 304 were formed as substrate which can resist successfully to mild condition (3.5 wt % of NaCl) in the chosen electrolyte medium. The analysis by FT-IR confirms the hybridization of gelatin and biopolymer of *k* -Carrageenan. The electrochemical results revealed that the coated SS 304 is a promising corrosion inhibition with an efficiency up to 97 % at 24h and up to 65% at 227 h. The E_{oc} values from open circuit potential analysis indicated the occurrence of passivation on the surface due to hybrid composite coating. Further, the electrochemical impedance spectroscopy showed that the resistance of hybrid composite is higher than the bare steel showing R_{ct} of $6.1 \text{ k}\Omega \cdot \text{cm}^2$ and $2.1 \text{ k}\Omega \cdot \text{cm}^2$, respectively. The microstructural analysis by

Scanning Electron Microscopy (SEM) and atomic force microscopy (AFM) confirmed that the coating surface have better corrosion resistance than SS 304 bare metal.

Keywords: *k*-Carrageenan; Red seaweed; gelatin; hybrid composite; stainless steel; corrosion inhibition.

1.Introduction

Protection of metal surfaces from corrosion by coating with polymeric hybrid/composite materials is consistent and efficient way of providing an impenetrable obstacle to the metal surface from water and other related corrosive species [1]. Solid adsorption of hybrid/composite materials on the active sites of metal surfaces can efficiently diminish the possibility of oxidation process by forming a protective film on their surface [2]. In this regard, the naturally occurring polysaccharides/biopolymers existing as the products of biochemical progressions in living systems [3]. Seaweeds signify a widely used source of different polysaccharides, well known in the industry for their food and sensor applications [4,5]. Red seaweeds produce carrageenans, agars, and variants, used in a manifold of industries as gelling and thickening agents. Polysaccharides, such as *k*-Carrageenans have significant industrial and biomedical relevance and shown several biological applications. Most importantly, ι -Carrageenan and κ -Carrageenan are also used in water-based paints due to their ability to prevent the settling of particles [6]. Recent reports state that the natural polymers have started to gain tremendous attention in corrosion inhibition due their availability, biocompatibility, non-toxicity and inexpensiveness [7, 8]. Such biopolymers, like *k*-Carrageenan can form complexes with metals by several active O donors in its heterocyclic rings which eventually shield metal surface from contact to corrosive medium [9]. Stainless steel 304 is widely used in many sectors of industry due to its high corrosion resistance and reusability [10]. The medicinal grade stainless steel is commonly employed as biomaterial in orthopaedic implants. Surface of SS304 can be modified to achieve antimicrobial feature by applying biopolymers through dip coating, brush coating or sol-gel coating [11].

Though several coating methods have been reported for improving the surface modification, especially conducting polymer coatings are continuously showing a great improvement for protection of metal surfaces [12,13] due to their strong oxidizing capability, the passivation of steel could be facilitated [14]. Significant numbers of environmentally friendly polysaccharides especially based on Inulin and family of Carrageenan have been published as polymeric corrosion inhibitors towards investigated for mild steel in 0.5

mol/dm³ H₂SO₄ [15]. The naturally available biopolymers have been utilized as an insulating layer to protect the metals from corrosion and preventing the electron transfer from the metal surfaces [16]. The *k*-Carrageenan derived from red algae, *Acanthophora spicifera*, consists of three hydroxyl and one sulfate groups. Its structure may bind with the metals and form complexes [17]. This green corrosion inhibitor can be combined with gelatin, known from good barrier properties, to provide enhanced corrosion resistance.

In the present work, corrosion inhibition as a hybrid conjugate between biomolecules of *k*-Carrageenan and gelatin was developed. Then, the formed coating barrier on the surface of SS304 were subjected to the mild electrolyte environment of 3.5 wt. % NaCl. Corrosion rate and the inhibition efficiency were determined using electrochemical techniques. The surface degradation of the polymer coated SS304 was examined using scanning electron microscopy (SEM) and atomic force microscopic (AFM) techniques. The results gathered in this research are paramount important in the biomedical field in which the corrosion degradation play an important role.

2. Materials and Methods

2.1 Materials collection

The red seaweed *Acanthophora spicifera* was collected at Central Marine Fisheries Research Institute, Mandapam region of Ramanathapuram district, (lies between 9°5' and 9°5' North Latitude and 78°1' and 79°27' East Longitude) Tamil Nadu, India. The medical- grade stainless steel (SS304) (chemical composition of SS0304 (wt. %) Cr-18.18%, Si-0.57%, Mn-1.75%, P-0.028%, C-0.051%, Ni-8.48%, N-0.05%, S-0.005%, Fe-70.886%) was purchased from Alfa-Aesar, Thermo Fisher Scientific India (P) Ltd, Mumbai, India. Gelatin, NaCl, and emery sheets (300-1000 grit) of GR grade were procured from Sigma Aldrich, India.

2.2 Extraction of *k*-Carrageenan polymer

The collected red seaweed was subjected to the initial purification process: 1. washing in the running to elucidate the adsorped impurities such as salt and sand; 2. cleaning with the distilled water; 3. air dry. Once seaweed is dried, it was grounded to a fine powder using mortar and pestle. The grounded algae were treated with a mixture of 20% (V/V) acetone and 80% (V/V) ethanol to remove hydrophobic and hydrophilic pigments. About 100 g of the purified seaweed was heated in 1000 mL of water at an alkaline pH (8-9) (0.5 mol/dm³ NaHCO₃) solution in a water bath at 90°C for 3 h, the existing insoluble residues were

removed by filtration. The filtered solution was precipitated with excess ethanol and dried at RT for 24 h, further grinded into fine powder yield 5 g of *k*-Carrageenan powder [18].

2.3. Carrageenan-gelatin coating Preparation

The *k*-Carrageenan-gelatin hybrid composite was prepared by the sol-gel method. The *k*-Carrageenan solution was prepared by dissolving 1 g of carrageenan powder in 10 mL of Milli-Q water kept under stirring for 30 minutes at 40°C at 700 rpm on a hot plate stirrer using a magnetic stirrer bar. Similarly, dissolving 1 g of gelatin granules in 10 mL of Milli-Q water at 50°C with constant stirring at 600 rpm for 30 minutes. The cross-linker was prepared by mixing 1 mL of glutaraldehyde in ethanol with 0.1 mL of HCl (0.01 N). The above two solutions were blended with the addition of the cross-linkers at 45°C for 20 minutes by magnetic stirring at 200 rpm [19,20].

2.4. Electrochemical Measurements

The SS304 surface (10 mm × 10 mm × 3 mm) was abraded with a series of emery papers (grade from 300-1200) and wash with water and acetone. 100 µl of *k*-Carrageenan - gelatin composite was formed on the SS 304 surface (10 mm x 10 mm) with a thickness of 0.5 mm using self-assembled multiple layer film by brush coating method [21, 22]. The enhancing barrier properties of the hybrid composite coating on SS304 were analyzed up to 227 h in a 3.5 wt % NaCl electrolyte solution. The corrosion studies were performed on CHI 760-CH, USA Instruments. The three- electrode setup, Ag/AgCl (3 M KCl), Pt wire and the biopolymer coated SS304 were used as a reference, counter, and working electrodes respectively. The test specimen (10 mm × 10 mm) was immersed in 3.5 wt % NaCl corrosive environment further, the standard corrosion tests including open circuit potential measurements (E_{oc}), electrochemical impedance spectroscopy (EIS) and Tafel polarization experiments. ASTM D 570- 98 standard was carried out to evaluate the corrosion inhibition efficiency. Further, the corrosion protection efficiency ($\eta\%$) of coated SS 304 metal was determined as in the earlier report [23]. The surface coverage was calculated by the formula described earlier in [24]. The corrosion rate of bare and coated SS304 was calculated by the following formula.

$$IE \% = R_{ct(C)} - R_{ct(B)} / R_{ct(C)} \times 100 \quad (1)$$

$R_{ct(C)}$ = Biocomposite coated in SS304 surface

$R_{ct(B)}$ = Bare SS304 surface

2.5 Surface analysis

FT-IR spectral analysis was carried out (Shimadzu – IR Tracer-100) to confirm the functional group of *k*-Carrageenan and gelatin biopolymers in the hybrid composite.

2.5.1 SEM and AFM Analysis

The surface characterization of SS304 (10 mm × 1mm × 3 mm) before and after the experiment coating with biocomposite and uncoated were fully immersed in 3.5 wt % NaCl for 227 h. The steel specimen was removed washed with distilled water and dried before the microscopic analysis. The scanning electron microscopy (VEGA3 TESCAN model) and Atomic force microscopy nanosurf ECSCAN 2 the model with cantilever ContAl-G – Switzerland.

3. Results and Discussion

3.1 FT-IR spectra of *k*-Carrageenan-gelatin

Figure 1 shows the FT-IR spectrum of *k*-Carrageenan and gelatin. The presence of sulfated polysaccharide indicates the stretching vibration at 1184 cm⁻¹ [25]. The vibrational band at 3466 cm⁻¹ confirms the presence of the hydroxyl group in the biopolymer carrageenan [26]. The band at 849 cm⁻¹ is assigned to the existing moiety in D-galactose-4-sulphate and 3,6-anhydrous-D-galactose [27]. Figure 1b displays the absorption peak at 3429 cm⁻¹ and 3404 cm⁻¹ attributed to N-H stretching vibrations of the amide group in gelatin, which is closely comparable with the previously reported pure gelatin [28,29]. The C-H stretching band is observed at 2923 cm⁻¹. The appeared sharp band at 2854 cm⁻¹ is attributed to the S-H stretching vibration band indicating the thiol group. The strong band observed at 1635 cm⁻¹ may be assigned to C=C stretching vibrations [30].

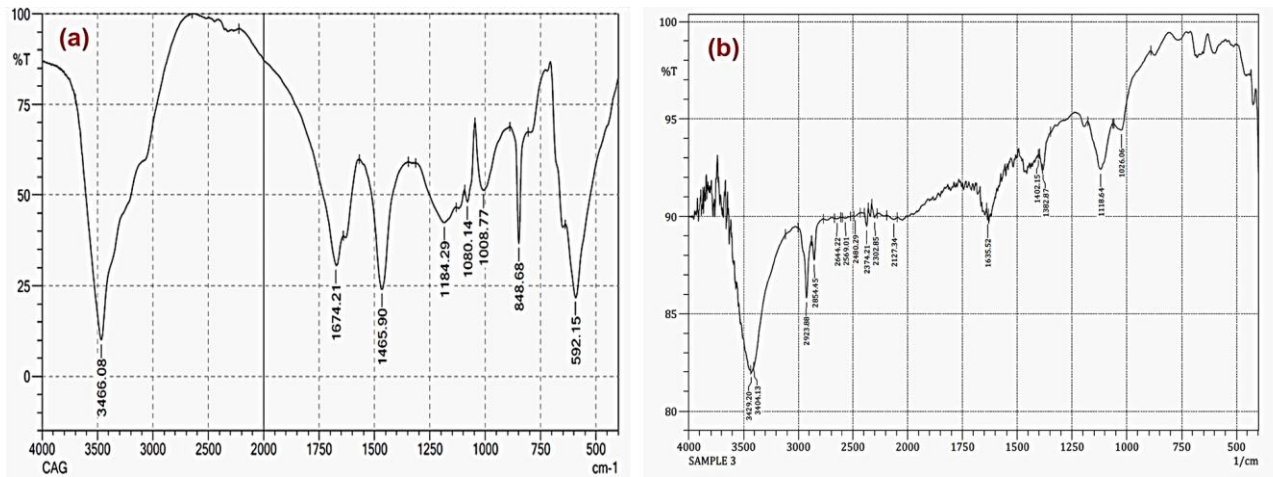


Fig.1. FTIR spectra of (a). Seaweed extracted carrageenan polymer and (b) gelatin

3.2 Electrochemical analysis

The comparable preliminary E_{oc} and representative Tafel and EIS data towards bare SS304 are shown in Figure 2. The observed variation in E_{oc} may due to surface passivation (more positive E_{oc}) and its subsequent rupture (negative E_{oc}). This positive E_{oc} of the biocomposite coated film with respect to bare SS, suggested that the coating enable a better resistance to corrosion inhibition.

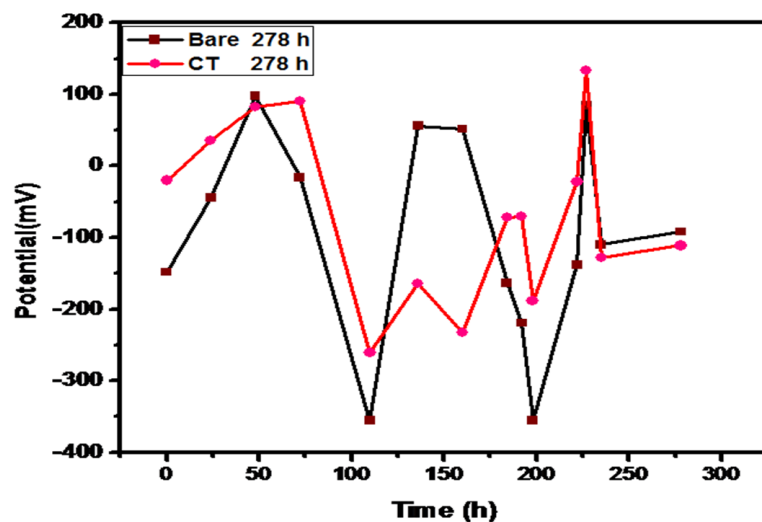


Fig.2. Open circuit potential (E_{oc}) vs time for bare SS and biocomposite coated SS at 278 h

This analysis helped us to identify the most favourable conditions for bare SS 304 which is at 47 h (98 mV) and 135 h (53 mV) and for biocomposite coated SS. However, considering the magnitude, the biocomposite has a more positive E_{oc} (134 mV) than bare SS (82 mV) at 227

h. Further variations observed in E_{oc} towards negative potentials for coated SS 304 at 136 h (-166 mV) and 58.3 mV for bare SS. for biocomposite coated surface suggested the occurred rupture and breakdown of the passive film, again the passivation was noted on the biopolymer coated film at 190 h (-70.8 mV) compared to the bare SS304 (-219 mV) [31]. The variation of E_{oc} with respect to time is shown in (Figure 2). It may be noted that the E_{oc} values of both bare SS and biocomposite coated SS showed a periodic variations in both positive and negative directions, suggested that the continuous passivation by forming a film on the surface and its subsequent failure, and such behaviour is very common in SS surface [32]. The rapid and random variations in E_{oc} may be attributed to the percolation of the electrolyte ions (chloride ions) into the interface, which is likely to be promoted by the porosity of *k*-Carrageenan–gelatin hybrid composite coating on SS. However, observing the trend in the variation (Figure. 2) and based on the sign and magnitude of E_{oc} , the biopolymer/SS composite showed a more positive values of -22 mV at 0 h, and 134 mV at 227 h than bare SS at 0 h (-148 mV) and 227 h (82 mV) [33]. The detailed information about cathodic and anodic tafle slopes, polarization resistance and corrosion rate of bare and composite coated samples at different times 0 h, 24 h, 96 h, 192 h and 227 h were presented in Table 1 and Table 2.

Table 1. Electrochemical data for the biocomposite coated SS304 and Bare SS 304 in 3.5 wt % of NaCl as electrolyte

S.No	Time (h)	Bare /Coated	E_{corr} (mV vs SCE)	I_{corr} ($A\ cm^{-2}$)	β_c (mV/dec)	β_a (mV/dec)	R_p (cm^{-2})	C_R (mmpy)
1.	0	B	188	3149×10^{-3}	1007	8836	124649	10.01
		C	408	1821×10^{-3}	2809	6651	470916	5.79
2.	24	B	162	1746×10^{-3}	3081	199	464871	5.55
		C	269	2691×10^{-4}	260	455	2669	8.55
3.	96	B	591	1286×10^{-3}	4391	4855	792059	4.08
		C	165	1277×10^{-3}	814	7537	253576	4.06
4.	192	B	484	5487×10^{-3}	3131	6047	8055	17.44
		C	638	2190×10^{-3}	834	5361	1430	6.96
5.	227	B	302	8753×10^{-4}	1948	6590	476.8	27.8
		C	653	8108×10^{-4}	3943	4776	1628	25.7

B. Bare SS304 specimen

C- Biocomposite coated SS304 specimen

Table.2 Electrochemical impedance parameters for bare SS 304 and biocomposite coated SS304 in 3.5 wt % NaCl electrolyte.

Time (h)	R_{ct} (Bare) Ω cm²	R_{ct} (coated) Ω cm²	% IE
0	94.8	223.8	57.65
24	25.84	1238	97.91
96	48.03	327.8	85.34
192	473.42	1052	55.98
227	2141	6035	64.52

R_{ct}- charge transfer resistances (Ω cm²)

3.3. Potentiodynamic polarization curve

The anodic and cathodic tangent were observed in Tafel plot. The multilayer biocomposite coating could be effectively sealed the pores and protects the surface of SS304, which was shown in Tafel data, as illustrated in Figure 3b, the detailed cathodic and anodic protection results have been reported in the presence and absence of biocomposite coating. The more favourable shift in E_{corr} values towards positive direction for the biocomposite coated SS (-269 mV) and bare surface (162 mV). The biocomposite acts as barrier molecules and blocking the surfaces of SS304 from corrosion [34]. The decreasing I_{corr} values were observed at 24-96 h. The protective coating forms on the surface of SS304 by the active functional groups such as amino group (-NH₂) in gelatin and sulphates (SO₄²⁻) in *k*-Carrageenan polysaccharides. These active functional groups of biocomposite are enhancing the anticorrosive properties and efficiently catalyze the oxygen reduction on the metal surface. Generally, the Tafel plots have shown less E_{corr} values (<85mV) for biocomposites coated SS304, which indicates that the polysaccharide polymers could efficiently inhibit the anodic and cathodic reactions on the surface of SS304 [35].

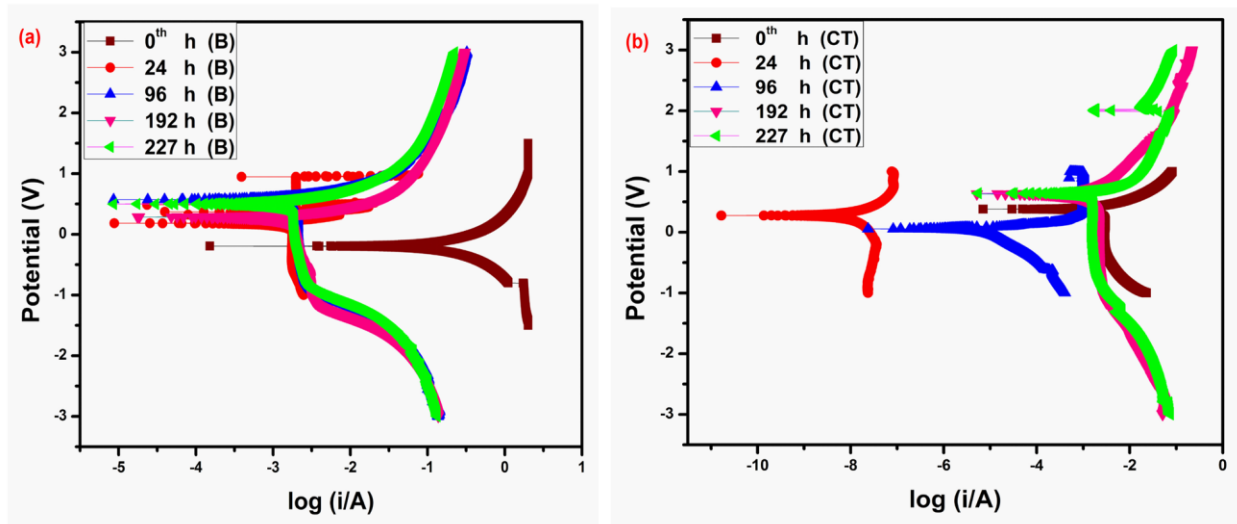


Fig.3. (a) Potentiodynamic polarization curve for bare SS and b) biocomposite coated SS 304, respectively.

3.4. Impedance spectroscopic analysis

The corrosion inhibition efficiency was further confirmed by electrochemical impedance spectroscopic technique (EIS) using CHI 760-CH, USA, Instruments with Z SimpWin software. The adsorption of biocomposite as film on the surface is represented in Figure 4 (a and b). The Nyquist plots of bare and biocomposite coated SS304 showed the occurred short depressed semicircle on bare SS304 throughout the scan and a higher R_{ct} value, which leads to obtain a long semicircle like graph for the coated SS304. The estimated corrosion inhibition efficiency of biopolymer coated SS304 is 65% at 227 h, which indicates that the biopolymer coating acts as a proficient barrier between metal surface and the corrosive environment [36]. The obtained percentage of impedance efficiency (IE%) is calculated according to Eq. (1) with the observed impedance results.

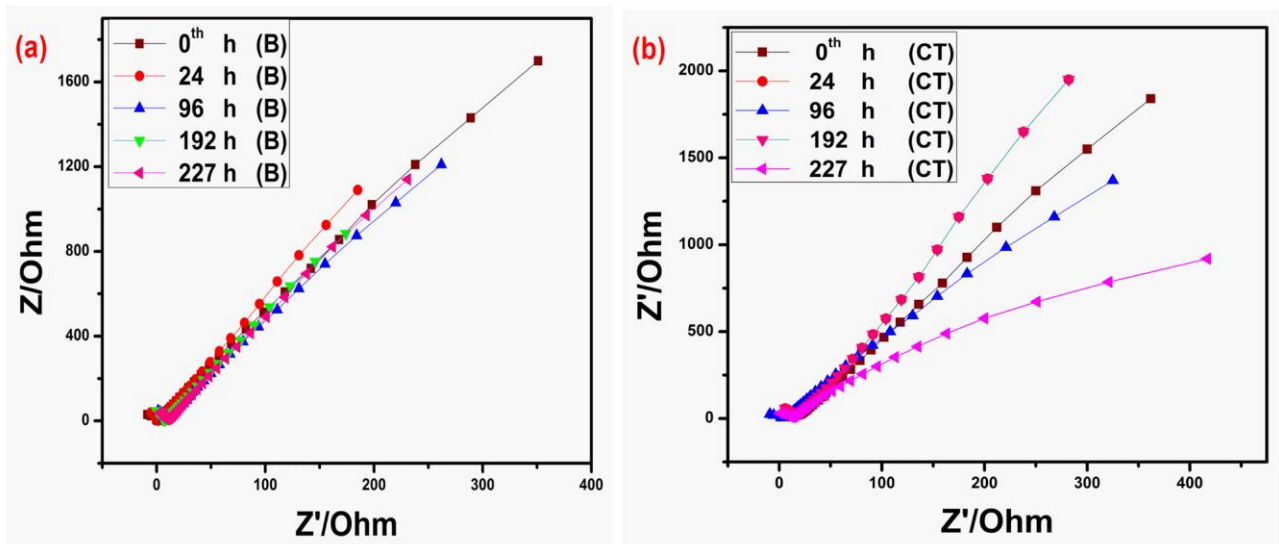


Fig.4 a) EIS (Nyquist plot) data of bare SS 304 and b) biocomposite coated SS 304, respectively.

The highest R_{ct} value ($1238.5 \Omega \text{ cm}^2$) was observed for biocomposite coated film, the corrosion rate was controlled by the charge transfer process. Where $R_{ct (CT)}$ and $R_{ct (B)}$ are the charge transfer resistances in biocomposite coated and bare SS304 respectively in 3.5% NaCl electrolyte. Roman et al., has reported passive layer formation on the surface of steel indicates the increased R_{ct} values [37]. The increased R_{ct} values was noted ($1238 \Omega \text{ cm}^2$) at 24 h, which indicates the passive layer formation and the corrosion inhibition efficiency was also noted as 97% and 65% inhibition efficiency was observed in 227 h. The decreased R_{ct} values was ($1052 \Omega \text{ cm}^2$) noted at 192 h, indicates the breakdown of passive layer and the diffusion of chloride ions into the surface [38]. Literature noted the increased charge transfer resistance (R_{ct}) was observed with increased concentrations of gelatin inhibitor. Gelatin is a good corrosion inhibitor, it forms a film on the surface of carbon steel, which protect the metal from the corrosion media [39]. The observed electrochemical impedance results denoted that the increased diameter of semicircle directly indicates the resistance of the sample. Corrosion resistance controlled by single charge transfer process [40]. The Nyquist plots obtained with increasing diameter indicate the response carrageenan and inulin biopolymer inhibitors.

3.5. Mechanism of corrosion inhibition

The obtained results showed that the proposed *k*-Carrageenan based hybrid composite with gelatin shows a remarkable inhibition efficiency towards the medical grade stainless steel 304 from the corrosive environment, attributed to their gel forming ability. The presence of

oxygen and electrostatically negative half-ester sulphate groups are strongly anionic and comparable to inorganic sulphate ions. These may serve as adsorption centres in the prepared composite which causes for the enhanced inhibition efficiency [9]. The obtained large passive domain of mild steel obtained by polarization curves in 0.5 mol/dm³ of NaCl containing nitrate ions at basic pH suggests the presence of Fe(II) oxides/hydroxides, as Fe₃O₄ and Fe(OH)₂. The SO₄²⁻ ions are fascinated by the charges on the metal surface which tends to be charged negatively. The obtained results could be explained on the hypothesis that the negatively charged SO₄²⁻ would attach to the positively charged metal surface. Such positively surface can electrostatically attract the negatively charged sulphate ions and the partial negatively charged oxygen heteroatoms of *k*-Carrageenan yields as adsorbed layer on the metal surface [41]. Schematic representation of adsorption of *k*-Carrageenan on mild steel surface is shown in Figure 5. Moreover, the gelatin molecules are anticipated to adsorb on the steel surface by an interaction with its nitrogen and oxygen atoms on the metal surface to form a metal/gelatin complex on the metal surface, which also facilitated the formation of *k*-Carrageenan based hybrid composite as a layer, which protects the steel from the corrosive environment under the experimental conditions [42].

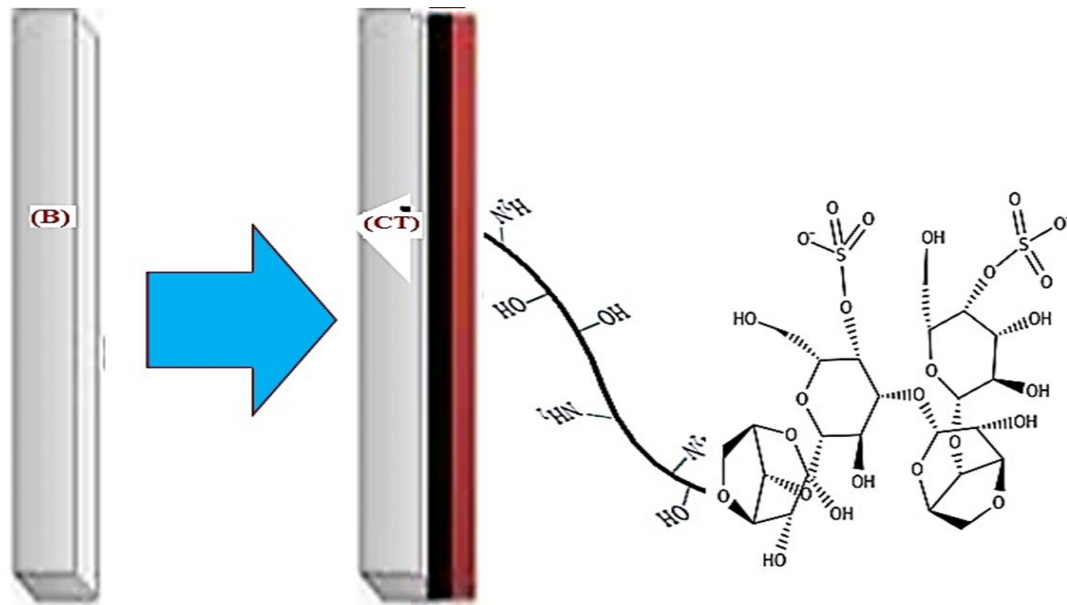


Fig.5.Mechanism of corrosion inhibition by *k*-Carrageenan-gelatin biocomposite

3.6 Surface morphology analysis

3.6.1 Scanning electron microscopy

As illustrated in Figure 6, the subsequent surface morphological changes of the bare SS304

and biocomposite coated thin films have shown smooth and devoid shapes on before and after the electrochemical studies with 3.5 wt.% of NaCl.

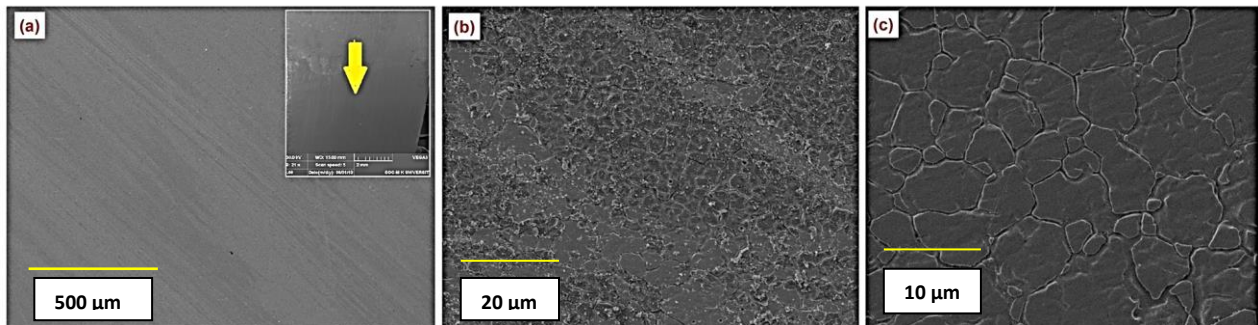


Fig. 6. SEM images of surface degradation of SS304 exposed to 3.5% NaCl electrolyte (a) biocomposite coated SS304 (inset image denotes the coating direction of SS304) (b) biocomposite coated SS 304 exposed to 3.5% NaCl electrolyte at 227 h (c) bare SS 304 exposed to 3.5 % NaCl electrolyte solution at 227 h.

The inset in Figure 6a depicts the carrageenan-gelatin coating direction on SS304. The observed morphological changes on SS304 indicates that the efficiency of barrier protective effect of biocomposite on coated SS304 (Figure 6b). The surface shows the deteriorate etched and devoid pitting on the surface damage after the immersion for biocomposite coated surface at 227 h. While, the bare surface of SS304 showed major scratches and severe damages with devoid pitting corrosion on the surfaces. These observed results confirm that the proposed novel biocomposite system acts as an effective barrier in protecting the SS304 in order to prevent penetration of ions and electrolyte into the steel sample [43].

3.6.2. AFM analysis

Figure 7 shows the surface morphology of three dimensional (3D) cross sectional AFM images of bare and biocomposite coated SS304. The surface roughness was calculated from the deviations in height to the profile mean value [44]. The surface of bare SS304 clearly shows a higher roughness value than biocomposite coated SS304 (Figure 7a). The estimated average roughness value for bare SS304 is 77.07 nm and the biocomposite coated surface roughness value is 49.61nm. The bare SS304 was effectively affected by the NaCl ions, due to their ease diffusion on the surface (see details on Figure 7 (a-b) [45,46]. The lower roughness values of biocomposite coated SS304 indicated an increase on the surface protectiveness under the corrosive environment.

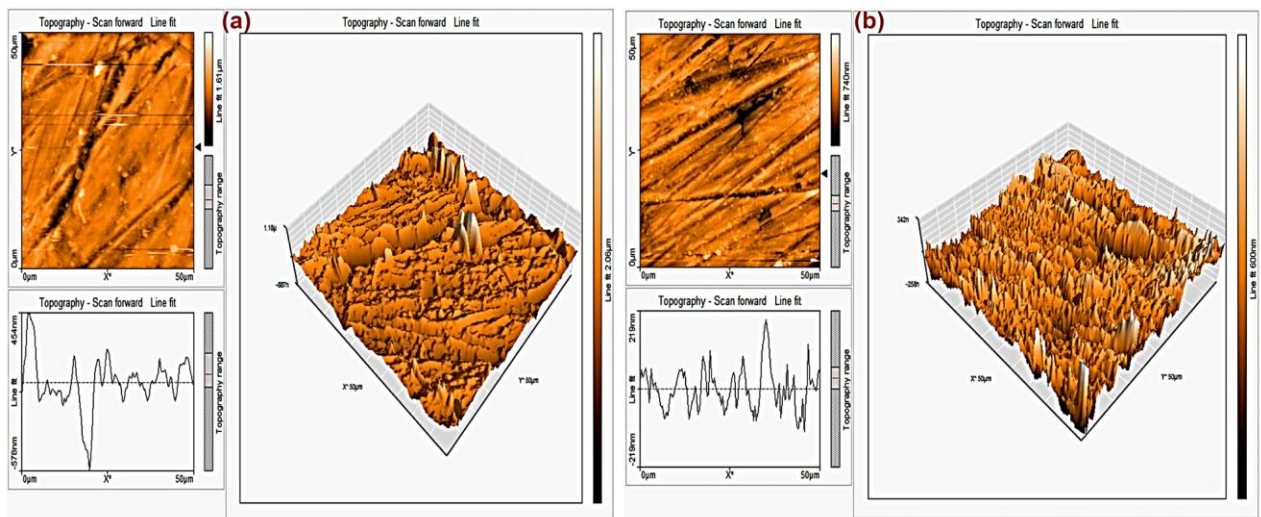


Fig.7. AFM images of (a). bare SS304.and (b) biocomposite coated SS304 after exposing 227h.

4. Conclusions

This novel study was focused to improve the surface of SS304 creating self-assembled multilayer coating using a gelatin cross-linked *k*-Carrageenan film. Its corrosiveness efficiency was evaluated by applying electrochemical technique in 3.5 wt. % of NaCl electrolyte. The observed two positive potentials at 87.29 mV (73 h) and 134 mV (225 h) for the biocomposite coated SS304 confirms its enhanced inhibiting property when compared to the bare specimen. The bare specimen showed lower potentials at -14.309 and 82.59 mV. Almost 65% higher corrosion inhibition efficiency were obtained with *k*-Carrageenan-gelatin composite by using potentiodynamic polarization, electrochemical impedance spectroscopy and open circuit potential analysis in 3.5 wt % NaCl. Further, the I_{corr} values from Tafel plot indicated lower values obtained for bare SS 304 subject5ed to longer time. It is concluded that the steel with biocomposite coating enabled better (above 95% corrosion inhibition efficiency) at the very beginning of the test. This may suggest that the biocomposite material with anticorrosive ability can be used as corrosion inhibitors, but the coating do not last for a long period when subjected to corrosion. Further a significant difference was noted when was compared the morphological structure of the bare and coated SS304 one. The AFM images revealed a decreased surface roughness for SS304 coated (i.e. 49.61 nm). The Scanning Electron Microscopic images indicated the occurrence of voids/cracks on the surface of bare SS304 while on the biopolymer coated SS304 were noted only mild pitting on the surface. The obtained results confirmed that the biopolymer composite *k*-Carrageenan-gelatin acts as a good protective film against corrosion progression. This novel coating

represents a cost-effective solution and act as an efficient corrosive inhibitor in practical usages. In the future, in order to further endorse the benefits of proposed coating (k-Carrageenan-gelatin) we want to verify its characteristics against recent coating materials proposed in the literature as anticorrosive agents for biomedical implants (see details of potential coatings in Table 3).

Table 3. Different coating materials as anticorrosive agents

S.No	Name of coating materials used for corrosion protection in biomedical applications	References
1.	Polydopamine Biopolymer	[47]
2.	Poly(lactic acid) and fluorine-doped hydroxyapatite	[48]
3.	Calcium phosphate	[49]
4.	Hydroxyapatite	[50]
5.	Antibacterial coating	[51]
6.	Silver-doped antibacterial CDHA	[52]
7.	MAO/PLA	[53]
8.	Sodium Alginate	[54]
9.	Pectin-grafted polyacrylamide	[55]
10.	Polydopamine/dicalcium phosphate dihydrate/collagen composite	[56]
11.	Mg ₂ Ca	[57]
12.	Hydroxide/poly-dopamine composite	[58]
13.	Polydopamine/liposome	[59]
14.	Dicalcium phosphate dihydrate/poly(lactic-co-glycolic acid) hybrid coating	[60]
15.	Poly(aniline-co-o-toluidine) copolymer	[61]
16.	Graphene + CeO ₂ + polyurethane	[62]
17.	Graphene + polystyrene	[63]
18.	Ni-Zn-TiO ₂	[64]
19.	Nanocomposite coating	[65]
20.	Nanostructured chromium coatings	[66]
21.	Polyurethane nanocomposite	[67]
22.	Polydimethylsiloxane-titania nanocomposite coating	[68]
23.	Nano-hybrid	[69]

	epoxy as protective marine coatings	
24.	Titania and alumina nanoparticles sol-gel coating	[70]
25.	Polyurethane composite	[71]

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