

Optimization of an ecofriendly coating containing chitosan and gelatin as corrosion inhibitor of carbon steel grade E by Response Surface Method

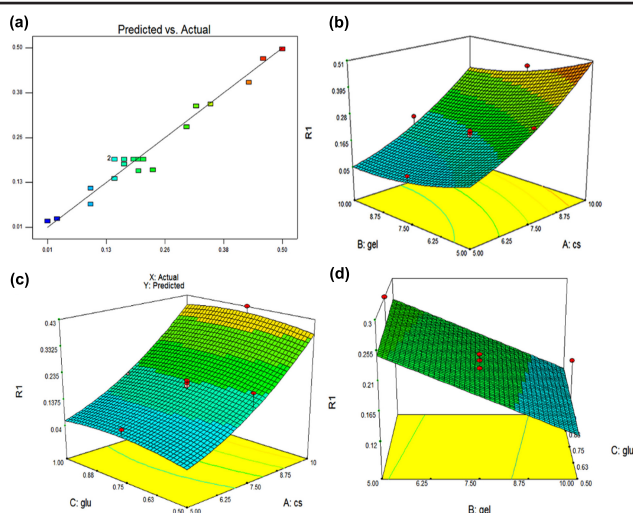
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HIGHLIGHTS

- Chitosan and gelatin biopolymers cross-linked with glutaraldehyde were used to cover the surface of carbon steel grade E.
- The cross-linker decreased water and ions from reaching the metal surface; thereby, increased the stability of the coating.
- The optimized coating can enhance the corrosion resistance of coated carbon steel up to 6 times.

GRAPHICAL ABSTRACT



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ABSTRACT

Corrosion can lead to tremendous defects, and several approaches are applied to alleviate the destructive consequences. In this study, two chitosan and gelatin biopolymers with glutaraldehyde applied as a cross-linker were used to cover the surface of carbon steel grade E. Results showed that a cross-linker decreased water and ions from reaching the metal surface; thereby, increased the stability of the coating. The experiment design was performed with Design-Expert 7.0.0 software and Response Surface Method (RSM) was used to optimize the concentration of chitosan, gelatin and glutaraldehyde. The coatings quality was investigated with microscopic image. Results showed that the optimum coating consist of 10 g.L⁻¹ chitosan, 5 g.L⁻¹ gelatin and 1 mL.L⁻¹ glutaraldehyde. Electrochemical Impedance Spectroscopy (EIS) test were done to compare the anti-corrosion property. The results demonstrated that this optimized coating can enhance the corrosion resistance of coated carbon steel up to 6 times. This can be attributed to a homogenous uniform coating on the metal surface confirmed with EIS. The scanning Electron Microscope (SEM) showed coating covered pores and scratches of bare coupon and the Atomic Force Microscope (AFM) corroborated the coverage of this composition on the carbon steel surface.

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1. Introduction

Corrosion, i.e. destruction or deterioration of a material because of reaction with its environment, is considered as a harmful industrial disaster. In 1960, The National Institute of Standards and Technology (NIST) estimated that the cost of corrosion for the United States is over \$300 billion. So, the use of reasonable beneficial corrosion inhibitor seems to be very vital. Although most of today's applicable inhibitors are hazardous and can contaminate the global environment, Green inhibitors show promise for the future. Polysaccharide-based biopolymers have shown high almost unlimited chemical stability [1]. In the last decades, use of environmentally friendly, renewable and specially polysaccharides have been considered [2]. These kinds of coatings are affordable and low toxic [3]. Chitin is the second most plentiful polysaccharide on the earth, it is known as an important structural element in the external shell of Crustaceans and can be found in squid, fungi, insects, spiders, shellfish, and some algae species [4]. Chitosan is derived from kinetic alkaline deacetylation of chitin. The deacetylation level rarely reaches 100%, so the level in which product is soluble in dilute acidic medium would be acceptable [5]. Potassium and NaOH are chemicals used for the deacetylation of chitin [6]. The chitosan most important functional group is the amine group. Nitrogen electrons present in the amine group can form a dative band with ion exchange metals [7] and block active corrosion sites [8]. Chitosan is widely used in drug deliverer systems [9], tissue engineering and as an antimicrobial agent [10]. The chitosan's ability to make a complex bond with metal's surface give an anti-corrosion property to this biopolymer [11]. Other features of this biopolymer are adaptability, anti-microbial activity, biodegradability and excellent ability to form films [12]. The profitable chitosan properties make it a promising corrosion inhibitor. The major problem of chitosan coating is the high absorption of moisture which makes it vulnerable. A dextrin-chitosan combined formation can reduce the hydrophobicity and subsequently provide higher coating strength [13]. When chitosan and tri methyl chitosan were used as corrosion inhibitor the corrosion efficiency increased 20-93% [14]. The application method of chitosan deposition on metal surface plays an important role in the coating protection ability.

Researchers report that the corrosion efficiency of chitosan for magnesium-calcium alloy depends on the chitosan molecular weight and the number of layers deposited on the surface [15]. An electroplated composite coating of chitosan/zinc oxide nanoparticles was used for carbon steel protection in aggressive corrosive medium [16-17]. In another research, the chitosan layer was placed between two layers of poly vinyl butyral and a layer by layer coating covered the surface of steel [8]. The authors showed that the chitosan corrosion inhibition in an acidic environment increases when increasing the concentration of chitosan and decreases with increasing temperature [18].

Adding gelatin to metal coating provides a great enhancement in coating anti-corrosion properties. Gelatin has been used as an additive to zinc-nickel alloys coating for steel in industries and anti-corrosion test results have proven it has a protective characteristic [19]. Gelatin has also been used as an additive for Fe, Zn, Zn-Fe and Zn-Fe-Ni coatings in industrial application and increased corrosion resistance [20].

Although authors have studied the corrosion protection ability of chitosan and gelatin separately, previous research has rarely focused on the interaction of these coating and consequent results. Here in this study, chitosan was used for the first time with two additives, i.e. gelatin and glutaraldehyde, to cover the surface of carbon steel grade E. Glutaraldehyde was used as cross-linker for chitosan to reduce chitosan water absorption and increase coating stability. Glutaraldehyde reduces the intramolecular hydrogen bonds of chitosan leaving more groups of hydroxyl and amines available to form chelate with metal ions. Electrochemical test results confirm the improvement of corrosion protection ability of the coated surface. SEM surface analysis was applied to prove the biopolymer formed a coating on the metal surface.

2. Materials and methods

2.1. Materials

Low molecular weight chitosan (Sigma Aldrich), and edible grade of gelatin were bought from Tetrachem (IRAN), glutaraldehyde 25% and acetic acid were procured from Merck. The percentage of elements used in the carbon steel consisted of 0.0941% C, 1.089%

Mn, 0.0104% P, 0.0067 S, 0.0165% Si, 0.0386% Ni, 0.0350% Cr, 0.0125% Mo, 0.0601% Ti, 0.0076% Co, 0.0493% Al and 0.278% Cu and its structural uniformity was measured by photometric analysis. In this study a Topsonic ultrasonic and Heidolph heater-stirrer was used to prepare coupons and solutions.

Coatings quality was investigated with Olympus-BX51 microscope images. The surface morphology of the biopolymer coated metal was characterized using a scanning electron microscope (SEM; VEGA\TESCAN, Czech Republic).

Corrosion study and coatings evaluation were done with electrochemical impedance spectroscopy (Biologic-VSP-300). First, each pre-treated sample was mounted on a holder as a work cell with saturated calomel and platinum electrodes as a reference and counter electrodes, respectively, as the circuit was prepared to run. Then an EIS test was conventionally accomplished in 10 mHz to 100 kHz frequency with an input AC voltage of 10 mV. Lastly, a 3 mm² circular area of cell was exposed to an aerated 3.5% NaCl aqueous solution electrolyte. Here, the prepared solution was poured on to the carbon steel coupon and placed under laboratory condition overnight to be deposited as a coupon coating with solvent evaporation. The coated samples served as the EIS work electrode.

2.2. Initial preparation of coupons

A carbon steel plate with a 4 mm thickness was cut in 2×2 cm² pieces. All the pieces were polished with different size emery papers (240, 400, 600, 800, 1000 and 1200) for further electrochemical and morphological studies.

2.3. Decontamination and surface cleaning

The pieces were washed with ultrasonics in acetone to remove fats and contaminants from the surface of the coupons. Then, they were washed with ethanol and distilled water and finally dried with sterilized napkins.

2.4. Optimization of coating compounds concentrations by RSM

The optimized concentration of chitosan, gelatin and glutaraldehyde 25% in coating was calculated during the comprehensive studies of response surface method (RSM) data.

2.5. Preparation the desirable coating

50 mL of twice distilled water was put on a heater-stirrer set at 40°C and 0.5 mL acetic acid was added. According to the experiment design by RSM, chitosan and gelatin were added to the solution. The solutions were stirred for two hours. Then, according to the Table 1 glutaraldehyde was added to the solutions. Each prepared solution was poured onto the carbon steel coupons placed on a separate plate. The plate containing the coupon and solution was placed under laboratory condition overnight to be deposited as a coupon coating with solvent evaporation.

3. Results and discussion

3.1. The response surface method (RSM) analysis

The response surface method was used to select the optimum concentration of coating materials. The surface morphology was carefully investigated via optical microscope images. The coatings were scored on the basis of their quality and these scores were given as a response to the software. Values of “Prob > F” less than 0.0500 indicate that model terms are significant. According to calculated data, A, B, A² are significant model terms. Although C is an insignificant term, it was considered in the calculations since C was one of the main factors. Values greater than 0.1000 indicate the model terms are not meaningful. Table 2 shows the new optimization results after using ANOVA analysis to eliminate insignificant terms.

The model F-Value of 72.44 implies the model is significant, but there is only a 0.01% chance that the “model F-Value” achieves this value due to the noise. The “Lack of Fit F-value” of 2.06 illustrates that the Lack of Fit is not significantly relative to the pure error. There is a 21.70% chance that a “Lack of Fit F-value” could have this quantity according to the noise. The Non-significant lack of fit is good. According to the contents and software results, the quality of anti-corrosion coating based on encoded factors (g.L⁻¹) can be calculated by Eq. (1).

$$R1 = +0.2 + 0.17 A - 0.06 B + 8 \times 10^{-3} C + 0.048 A^2 \quad (1)$$

Fig. 1a shows the quality of coating calculated by the relationship based on the actual amount of coating

Table 1. The RSM experimental design data to optimize the concentration of coating compounds.

No.	Chitosan concentration (g.L ⁻¹)	Gelatin concentration (g.L ⁻¹)	Glutaraldehyde concentration (mL.L ⁻¹)
1	7.5	7.5	0.75
2	7.5	7.5	0.5
3	5	10	1
4	7.5	7.5	1
5	7.5	10	0.75
6	5	5	0.5
7	5	7.5	0.75
8	7.5	7.5	0.75
9	5	10	0.5
10	10	10	0.5
11	7.5	5	0.75
12	7.5	7.5	0.75
13	7.5	7.5	0.75
14	10	5	0.5
15	10	5	1
16	10	7.5	0.75
17	7.5	7.5	0.75
18	10	10	1
19	7.5	7.5	0.75
20	5	5	1

quality. As illustrated in the figure, the difference between these two amounts is very low, which indicates a high degree of accuracy for the given relationship. Also, the scattering of data indicates the appropriate choice of factors and their levels.

According to Fig. 1b, in a constant concentration of glutaraldehyde of 0.75 mL.L⁻¹, increasing chitosan concentration from 5 to 10 g.L⁻¹ improved the quality

of the coating. But for the same case of glutaraldehyde, increasing the concentration of gelatin from 5 to 10 g.L⁻¹ decreased the quality of coating. Therefore, the optimum concentration for chitosan and gelatin at a constant concentration of glutaraldehyde (0.75 mL.L⁻¹) was 10 g.L⁻¹ chitosan and 5 g.L⁻¹ gelatin. According to Fig. 1c, in the case of fixed concentration of gelatin in 7.5 g.L⁻¹, increasing chitosan concentration from 5 to 10 g.L⁻¹ improved the quality of the coating. Also, increasing the concentration of glutaraldehyde from 0.5 to 0.75 mL.L⁻¹ enhanced the quality of coating but further increasing the concentration to 1 mL.L⁻¹ of glutaraldehyde decreased the quality of coating. Therefore, the optimum concentration for chitosan and glutaraldehyde at a constant concentration of gelatin (7.5 g.L⁻¹) was 10 g.L⁻¹ chitosan and 0.75 mL.L⁻¹ glutaraldehyde. According to Fig. 1d, in a concentration of chitosan fixed at 7.5 g.L⁻¹, increasing gelatin concentration from 5 to 10 g.L⁻¹ decreased the quality of the coating, but increasing the concentration of glutaraldehyde from 0.5 to 1 mL.L⁻¹ increased the quality of coating. Therefore, the optimum concentration for gelatin and glutaraldehyde at a constant concentration of chitosan (7.5 g.L⁻¹) was 10 g.L⁻¹ chitosan and 5 g.L⁻¹ gelatin.

The optimum response provided by the software is shown in Table 3. A solution was prepared with the optimum concentrations and was coated on the surface of carbon steel coupon.

3.2. Electrochemical Impedance Spectrometry (EIS)

EIS tests were carried out on an optimized coated coupon and a non-coated coupon as a control under aggressive NaCl 3.5% solution medium. In order to

Table 2. ANOVA analysis for response surface reduced quadratic model for optimization of chitosan, gelatin and glutaraldehyde coating after elimination of insignificant terms.

Source	Sum of squares	Degree of freedom	Mean squares	F-value	p-value	
model	0.33	4	0.082	72.44	< 0.0001	Significant
A-chitosan	0.28	1	0.28	247.1	< 0.0001	-
B-gelatin	0.036	1	0.036	31.9	< 0.0001	-
C-glutaraldehyde	6.4×10 ⁻⁴	1	6.4×10 ⁻⁴	0.57	0.4631	-
A ²	0.012	1	0.012	10.21	0.006	-
Residual	0.017	15	1.129×10 ⁻³	-	-	-
Lack of fit	0.014	10	1.365×10 ⁻³	2.06	0.2170	Not Significant
Pure error	3.283×10 ⁻³	5	6.567×10 ⁻⁴	-	-	-
Cor total	0.34	19	-	-	-	-

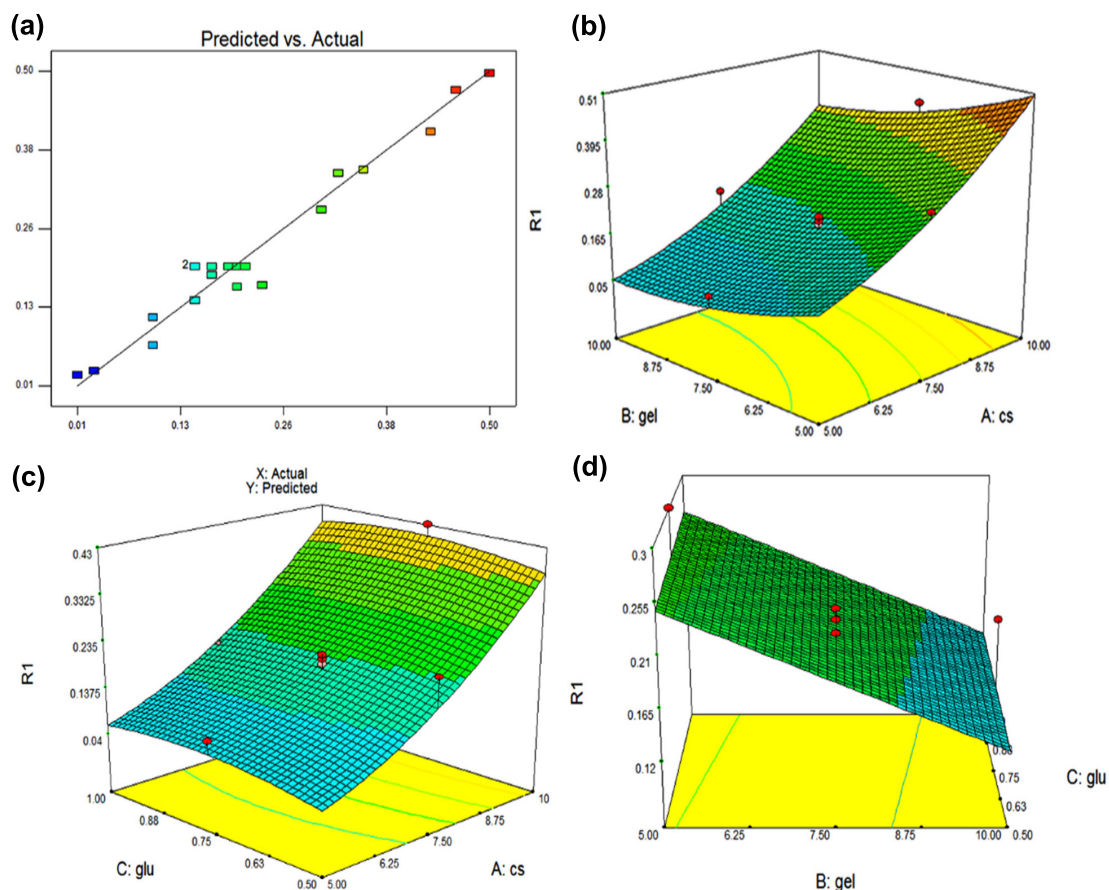


Fig. 1. (a) The difference between the qualities of the coatings obtained from the equation and real qualities of coatings. (b) Simultaneous effect of chitosan and gelatin at a constant glutaraldehyde concentration. (c) Simultaneous effect of chitosan and glutaraldehyde at a constant gelatin concentration. (d) Simultaneous effect of gelatin and glutaraldehyde at a constant chitosan concentration.

analyze the results of the EIS test, the simulation and fitting process was carried out with what is considered an appropriate equivalent circuit. Fig. 2 depicts the best fitted equivalent circuit used to obtain electrochemical data.

A one-time constant electrical fitted circuit proves that the charge transfer process dominantly handles the electrochemical events. The circuit consists of solution resistance (R_s), charge transfer resistance (R_p) and constant phase element of double layer (CPE_{dl}). The parameters were given in Table 4.

Double layer capacitance (C_{dl}), homogeneity parameter (h) and inhibition efficiency ($I.E.$ %) values can be calculated from polarization resistance via the following equation:

$$C_{dl} = (TR_p^{1-h})^{\frac{1}{h}} \tag{2}$$

$$I.E. (\%) = \left(\frac{R_p^* - R_p}{R_p^*} \right) \times 100 \tag{3}$$

where R_p^* and R_p are the polarization resistances of the coated and uncoated coupons, respectively.

Coating can make a corrosion resistant layer on metal surface to hinder the direct contact of aggressive species and consequent corrosion reactions. As illustrated in Table 4, the direct relationship of coating and resistant property is obvious. The decrease of C_{dl} shows the thickening of the electrical double layer and/or decrease of local dielectric constant. Typically, coating formation on a metal-solution interface reduces the electrical

Table 3. Concentration of coating material calculated via optimum response of software.

Chitosan (g.L ⁻¹)	Gelatin (g.L ⁻¹)	Glutaraldehyde (mL.L ⁻¹)	Response	Desirable conditions
10	5	1	0.48	0.959

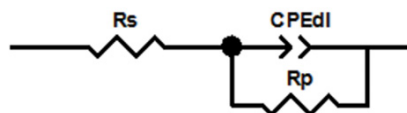


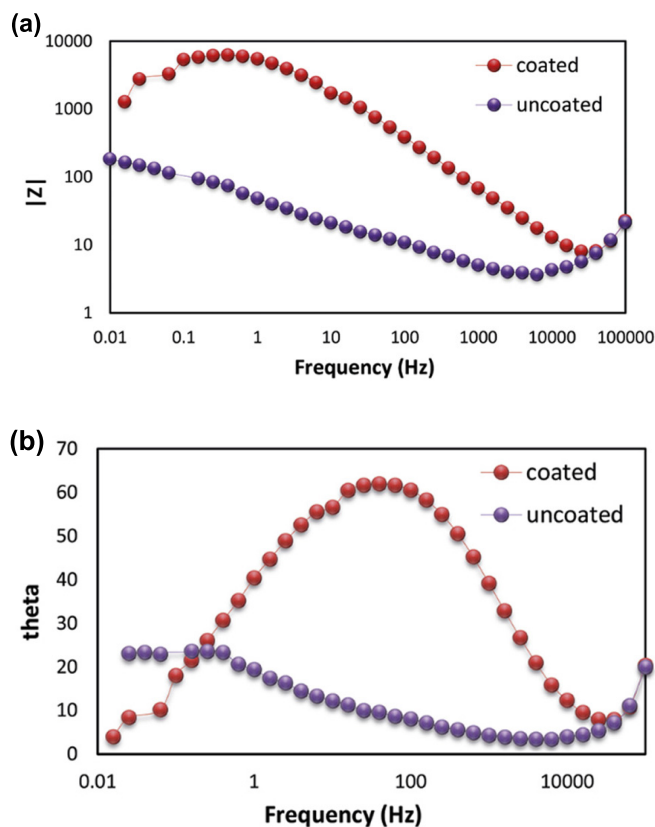
Fig. 2. Electrochemical Impedance Spectroscopy (EIS) best-fitted equivalent circuit diagram.

Table 4. Electrochemical impedance spectroscopy (EIS) kinetic parameters derived for coated and not-coated steel coupons

Sample	R_p ($\Omega \cdot \text{cm}^2$)	CPE_{dl-T} ($\mu\text{s n}\Omega^{-1} \text{cm}^{-2}$)	CPE_{dl-P}	C_{dl} ($\mu\text{F} \cdot \text{cm}^{-2}$)	$I.E. \%$
Uncoated	2861±85.4638	5.2543±0.2015	0.3464±0.0032	2.8868	-
Coated	19523±652.3415	0.021984±0.0008	0.7297±0.0064	1.3705	582.4

double layer resistance due to displacement of water molecules and other ions naturally adsorbed on the metal surface [21]. The higher homogeneity parameter (h) values in coated coupon reveals the decrease in roughness and inhomogeneity of surface [22].

Fig. 3 represents the Bode (a) and phase (b) diagram for coated and uncoated coupons exposed to 3.5% NaCl corrosive solution. Fig. 4 represents the Nyquist diagram of metal exposed to 3.5% NaCl solution under uncoated and coated conditions. In the Nyquist plot, the intercept of the EIS curve and x-axis (real impedance) is the electrolyte resistance, while the projected length of the EIS curve on the x-axis is the charge transfer. As shown in Fig. 4, the quaternary diameter of the coated coupon is much larger than the bare control coupon, which indicates that the corrosion resistance of the coated carbon steel is increased. This resistance depends on the thickness and density of the passive layer formed

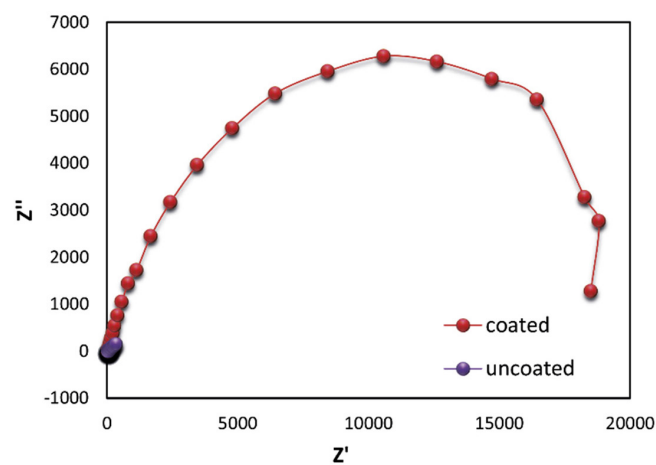
**Fig. 3.** (a) Bode and (b) phase diagram for coated and uncoated coupons exposed to 3.5 % NaCl corrosive solution.

on the surface of the sample. In the analysis of EIS diagram, it is assumed that the protective layer formed on the metal surface is compact, so the circuit of the equations is considered as RC in parallel circuits, so that the circuit electrical elements gained are indicative of electrochemical values.

To ascertain the reason for the vast difference in anti-corrosive property between the coated sample and the control sample, surface analyzing by scanning electron microscope (SEM) and atomic force microscope (AFM) was designed. Fig. 5 shows the top-view SEM images of these samples. Also, Figures 6 and 7 show the top-view AFM and 3D images of roughness, respectively.

The surface SEM photos indicate black pores and cracks all over the control surface (Fig 5a), while the coated coupon reveals a covered surface (Fig 5b). By blocking the corrosion species, the coating make a barrier layer on the metal surface. The protective layer reduced the corrosive medium-metal contact to a sufficient extent that the corrosion was prevented.

Surface AFM images reveal micro-structure dark scratches and grooves all over the control surface (Fig. 6a), while the coated coupon reveals a covered surface where the crystals of composition are visible (Fig. 6b). By blocking the corrosion species, the coating make a barrier layer on metal surface.

**Fig. 4.** Nyquist diagram for coated and uncoated coupons exposed to 3.5% NaCl corrosive solution.

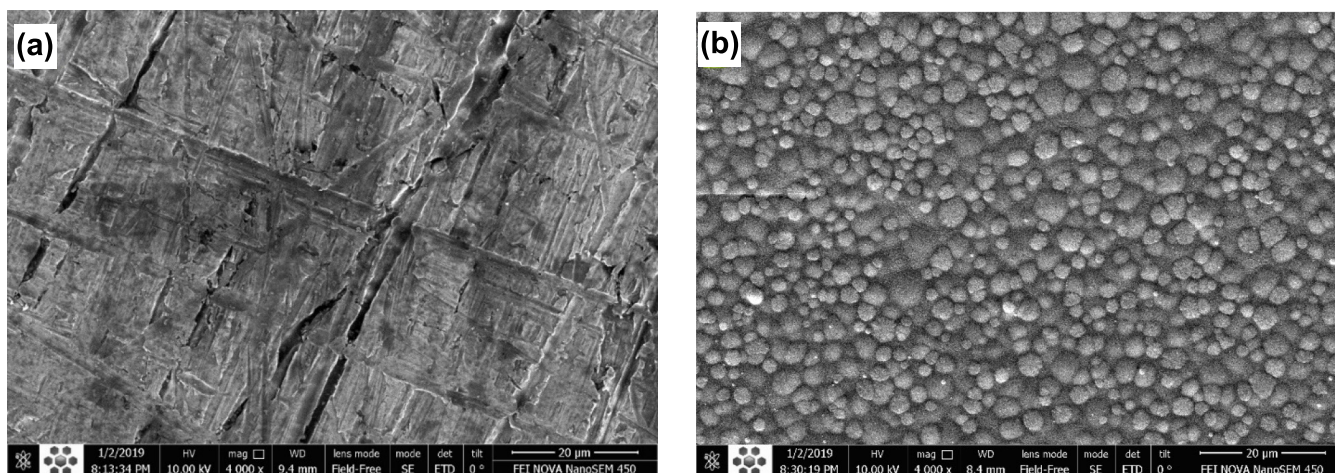


Fig. 5. SEM images of carbon steel coupon exposed to 3.5% NaCl corrosive solution, (a) bare carbon steel as control, and (b) coated with optimized solution.

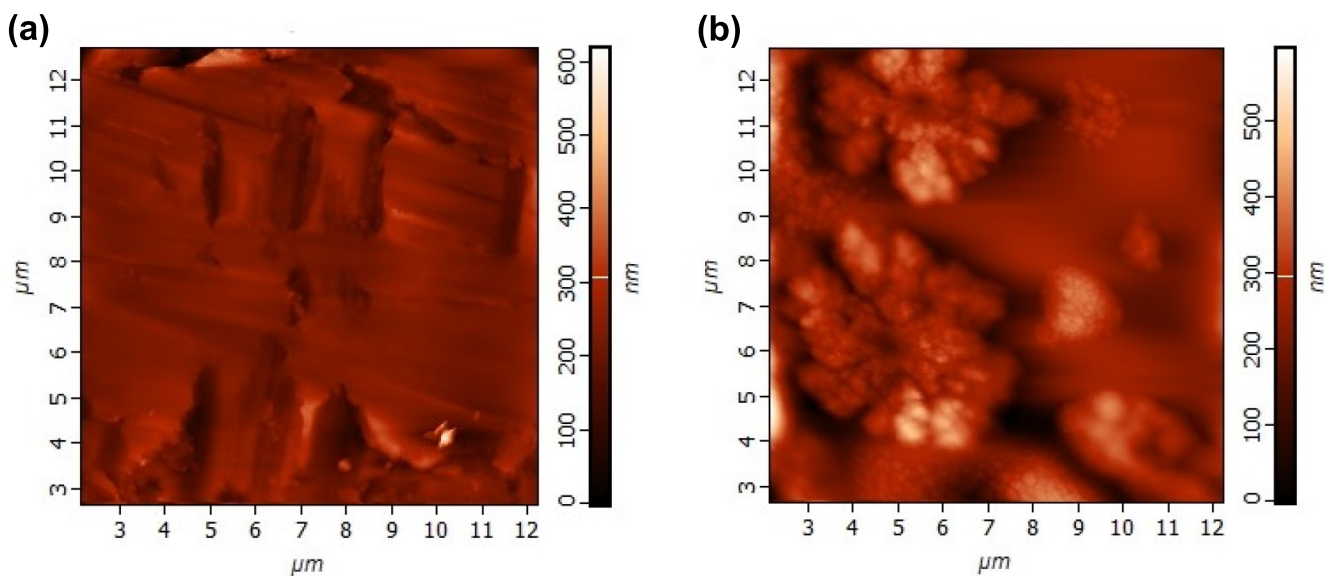


Fig. 6. AFM images of (a) bare carbon steel as control and (b) carbon steel coated with optimized solution ($10 \times 10 \mu\text{m}$).

Because the drying method leads to a greater thickness of the top layer formed on the surface, surface roughness increased compared to the control sample shown in AFM 3D images (Fig. 7). Statistic results showed that the average roughness of the coated sample was 49.74 nm and the control sample's average roughness was 26.83 nm.

In studies carried out in almost identical conditions (using chitosan to cover the surface of different types of steel), the maximum improvement in corrosion inhibition was about 100% in a study that used an acetyl thiourea chitosan polymer to cover the carbon steel surface (maximum $I.E.\%$ = 49.5) [23], the composite coating of chitosan/zinc oxide nanoparticles used for carbon steel (maximum $I.E.\%$ = 73.8[17], chitosan derivation was used to cover carbon steel (maximum

$I.E.\%$ = 92) [24], and chitosan with iodine ions covered the surface of stainless steel (maximum $I.E.\%$ = 99.72) [25]. In this study corrosion resistance improved about 6 times, which shows a great improvement in the resistance of the coating against corrosion.

4. Conclusion

A new type of corrosion inhibitor coating is reported in this study. The present study focused on an efficient green inhibitor for carbon steel grade E in 3.5 M NaCl environment. Due to its cross-linked structure, augmentation of glutaraldehyde in the chitosan and gelatin coatings resulted in a physical barrier that prevented water and ions reaching the metal surface. The corrosion inhibition of this coating, coming from

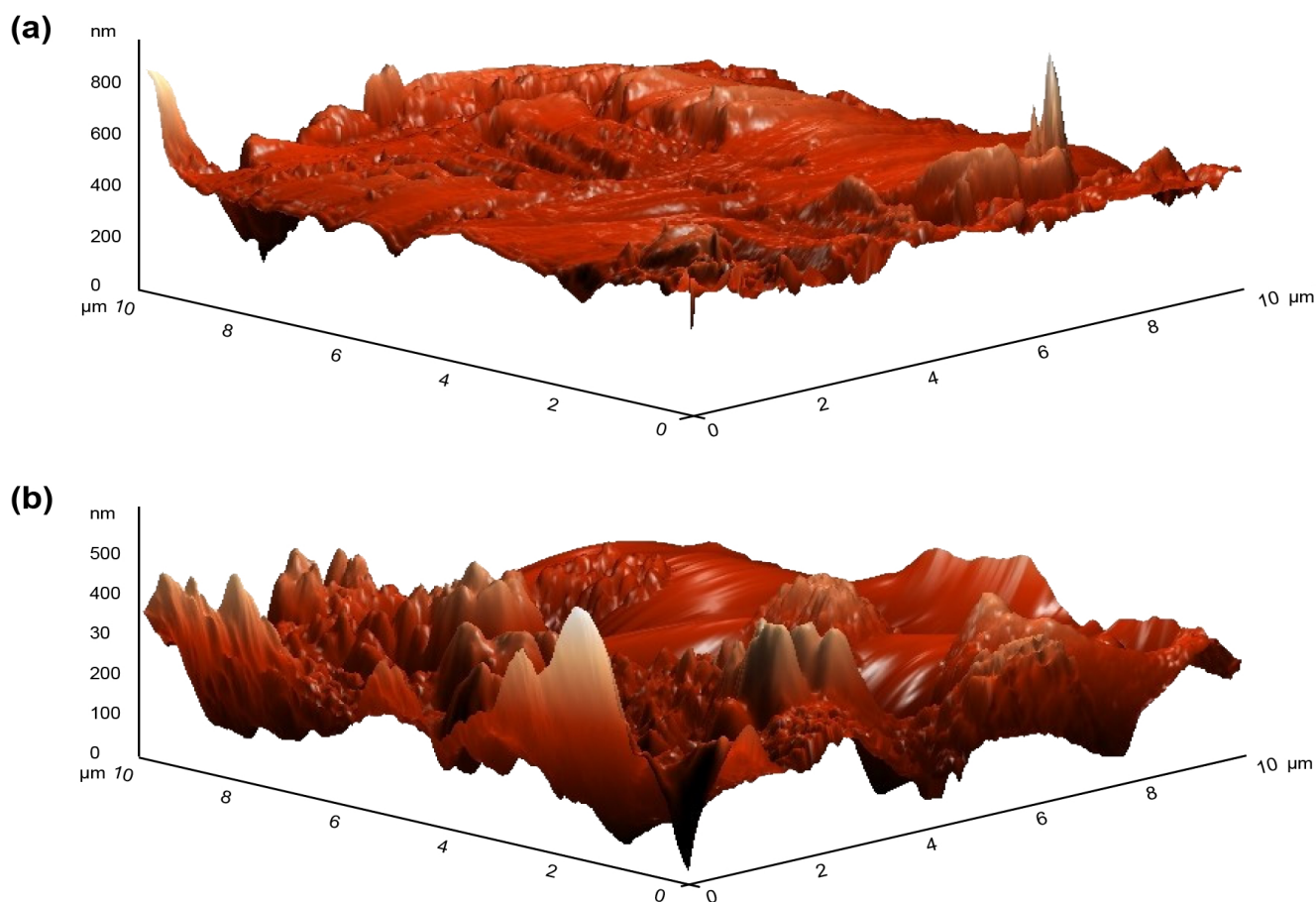


Fig. 7. AFM 3D images of (a) bare carbon steel as control and (b) carbon steel coated with optimized solution surfaces.

the interaction of metal ions with functional groups of chitosan and gelatin, was confirmed owing to the high Z-modulus at low frequency in the Bode plot. Experimental design with Design-Expert 7.0.0 software and response surface method was employed to optimize the concentration of components. RSM explains the influence and also the interaction between the factors. The optimal level of factors was found to be 10 g.L^{-1} of concentration of chitosan, 5 g.L^{-1} of concentration of gelatin and 1 mL.L^{-1} of concentration of glutaraldehyde. Electrochemical impedance spectroscopy (EIS) test was conducted on the coated and uncoated coupons, and results showed a better corrosion behavior of coated carbon steel in 3.5 M NaCl in comparison with bare one. The experiment at the optimized condition inhibits carbon steel corrosion in 3.5 M NaCl with 525% inhibition efficiency. This can be attributed to a protective film formed on the carbon steel surface which was confirmed with EIS and SEM. Due to the drying method which resulted in a greater thickness of the top layer formed on the surface, the surface roughness increased compared to the control sample as showed in AFM images.

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