THE EFFECT OF CULTURE MEDIUM NUTRIENTS CHANGING ON INHIBITION PROPERTY OF C. INDOLOGENES MUT.2 BACTERIAL BIOPOLYMER AS A NOVEL GREEN CORROSION INHIBITOR

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Recently the researchers have focused on using ecofriendly corrosion inhibitors for corrosion protection of metals against aggressive environment. Here, the corrosion inhibition property of Chryseobacterium indologenes MUT.2 bacterial biopolymer for carbon steel corrosion protection has been investigated. In this work, different culture mediums for bacterial cultivation were prepared and their probable effects on inhibition ability of produced biopolymers were investigated. Electrochemical studies with electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization using Tafel extrapolation technique were carried out in 3.5% NaCl corrosive solution. It has been shown that changing the culture medium constituents can influence the inhibition ability. Results indicated that the biopolymer produced in culture medium with cheese whey as carbon source have the most inhibition efficiency of 54%. The Biopolymer acted as a mix inhibitor and physically adsorbed on metal surface. The interaction between charged functional groups of biopolymer and charged corrosive species forms Fe-biopolymer complexes that deposits on metal surface and consequently reduce the rate of corrosion by lowering the direct contact of metal surface to aggressive solution.

Keywords: corrosion, biopolymer, culture medium, EIS test, Tafel test

1. Introduction

Metals can be easily corroded when they expose to corrosive medium. Corrosion can impose a great expense on industry. So, several approaches have been investigated to reduce the corrosion harmful consequences. The protection strength of applied corrosion control approach as well as the total operational cost, health and environmental considerations are the most important criteria to choose the effective protection method [1]. Using ecofriendly, non-toxic, cheap green corrosion inhibitors is a promising approach that recently has been focused.

Salghi et al [2] investigated the inhibition ability of the green tea extract (GTE) for C38 steel protection in 1 M HCl solution. The results showed that that

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GTE acts essentially as mixed-type inhibitor controlling cathodic and anodic reactions. Jokar et al [3] studied the corrosion inhibition of morus alba pendula leaves extract (MAPLE) (belong to the Moraceae family that mainly grows in east Asia) for carbon steel in 1 M HCl solution at different concentrations (0.1–0.4 g.L\(^{-1}\)) and temperatures (25–60°C). Results revealed that a high inhibition efficiency value of 93% was achieved in the presence of 0.4g.L\(^{-1}\) MAPLE at room temperature (25°C). Ostovari et al [4] studied the inhibitive action of henna extract (Lawsonia inermis) and its main constituents (lawsone, gallic acid, α-D-Glucose and tannic acid) on corrosion of mild steel in 1 M HCl solution. They showed that all the examined compounds act as a mixed inhibitor and inhibition efficiency increases with inhibitor concentration. Charitha et al [5] studied the protective action of biopolymer starch on 6061 Al-15%(v) SiC (P) composite in 0.25 M HCl with temperature ranging from 303 to 323°K. Maximum inhibition efficiency of 84% was observed at 323°K for 0.8g.L\(^{-1}\). They related the starch high inhibition to firm adsorption of the adsorbed inhibitor molecule onto the surface of the metal. Prabakaran et al [6] studied the inhibitive effect of Ligularia fischeri extract on the corrosion of mild steel in a 1 M HCl medium. The inhibition efficiency was observed to increase with increasing concentrations of Ligularia fischeri. A maximum inhibition efficiency of 92% was achieved using 500 ppm of the inhibitor. Prabhu et al [7] investigated the corrosion inhibition characteristics of aqueous extract of seeds of Coriandrum sativum L. for corrosion control of aluminum in 1 M phosphoric acid solution. The polarization studies showed that the CSE acted as mixed inhibitor and the inhibitor molecules physically adsorbed on the surface of aluminum.

Several types of green inhibitors have been studied to investigate their corrosion inhibition property. The studies are more concentrated on the inhibition properties of animal or plant extract inhibitors [2-11]. But the works on bacterial biopolymer inhibition property are so scarce [12] and therefore need to be more considered.

Due to their ability to form a high resistance layer on metal surface, biopolymers can be successfully regarded as the green corrosion inhibitors. The producing conditions of bacterial biopolymers such as their producing culture medium compositions and as well as fermentation process such as pH, temperature, oxygen concentration and agitation can severely affect the quantity
and quality of produced biopolymers [13-14]. The quantity of produced biopolymers is mainly related to fermentation process condition while the biopolymer quality (its chemical and physical characteristics) is nearly determined by its producing culture medium [15]. Optimization of biopolymer production conditions to reach the most amount of biopolymer has been subjected to significant studies [16-18], while their influence on the biopolymer performance has been rarely investigated [19]. The cost and reachability of biopolymer producing culture medium nearly determines the total cost of produced biopolymer [20]. There are a lot of approaches to alleviate the corrosion harmful consequences. The method that is used to reduce the corrosion defects can deeply affect the value of decrease in corrosion rate [21].

Here in this work, the corrosion inhibition of the C. indologenes MUT.2 bacterial biopolymer was investigated as an eco-friendly green inhibitor for corrosion control of carbon steel in 3.5% NaCl solution. Although the biopolymer showed the corrosion protection when used as a metal coating [22-23], but its capability to be effective in other corrosion control approaches had not been studied yet. So, the inhibitive action of bacterial biopolymer produced in different culture mediums was examined using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The functional groups of biopolymer were characterized by FT-IR analysis.

2. Materials and methods

2.1. Metal substrate

Carbon steel coupons were prepared in a 25 mm × 15 mm × 3 mm dimensions size. The metal composition was characterized by a quantometric test (Spark Emission Spectrometer, Germany). The percent weight composition of the coupons was 1.038 Mn, 0.0101 Si, 0.0423 Ni, 0.0344 Cr, 0.0075 Mo, 0.0044 S, 0.0102 P, 0.0812 C, 0.0517 Ti, 0.0081 Co, 0.0426 Al, 0.0275 Cu and the rest of Fe.

2.2. Coupons preparation

Coupons were carefully ground with different size emery papers to obtain the completely polished surface. The polished coupons were rinsed with deionized water and degreased with acetone in ultrasonic bath [24].

2.3. Bacterial strain definition

The Chryseobacterium indologenes MUT.2 strain was extracted from garden soil of Arak city in Iran. The isolation to recognition procedure was performed by Biotechnology Research Centre, Tehran, Iran. The strain was determined by Sequence analysis of 16S rRNA gene. The sequence is available at
gene bank database (NCBI) under JN831444. Chryseobacterium is a gram negative, catalase-positive, nonmotile, oxidase-positive, non-glucose-fermenting bacterium, indole-positive [22].

2.4. Biopolymer production

The inoculum having a minimum cell concentration of bacterial strain is necessary to initiate the bacterial activity in medium culture. C. indologenes MUT.2 strain cell was incubated in sterilized LB-broth in 30°C for 12 hr to prepare the inoculum solution. The solution was periodically sampled, and the cell concentration of prepared sample was monitored by PerkinElmer model Lambda 20. Cell concentration of 10^7 CFU mL^-1 was an acceptable point of cell growth.

Khani et al optimized the bacterial cultivation medium to reach the maximum biopolymer production value as: sucrose (21 g.L^-1), glutamic acid (20 g.L^-1), K2HPO4 (6 g.L^-1), NaH2PO4 (7 g.L^-1), NH4CL (0.7 g.L^-1), and MgSO4 (0.5 g.L^-1) [25]. They also reported that the amount of C. indologenes MUT2 produced biopolymer is highly related to the carbon and nitrogen sources of biopolymer production medium whereas the effect of other constituents is negligible [26]. Due to importance of the quantity of produced biopolymer in further industrial application, the assumption of choosing the carbon and nitrogen sources of biopolymer production medium as variable parameters for quality investigation seems to be reasonable. Recent studies on anticorrosion protection of C. indologenes MUT.2 biopolymer as a metal coating showed that the main effective criterion on protective properties was medium culture carbon source [23]. Showing the promising results when applied as a metal coating; the study on biopolymer probable ability to be used in another corrosion control approaches seems necessary.

Considering the above explanation, here for investigating the inhibitive action of biopolymer, one factor experimental design with substituting the carbon source of culture medium and constant nitrogen and mineral salt amount was regarded. Having reached to acceptable cell concentration, the inoculated culture medium (5%, v.v^-1) was added to sterilized prepared culture medium. The solution was incubated for 96 h in the orbital shaker (Tecnal mod.TE-424, Tehran, Iran) at 170 rpm. The incubated solution was centrifuged (Sigma 6–16 K, no. 12256) in 8000 g for 10 min to separate the desirable biopolymer from other solution constituents (biomass and other impurities). The obtained supernatant was mixed with chilled absolute ethanol. The biopolymers were precipitated after settling the mixed solution for 24h in 4°C refrigerator. Triple cultivation was carried out in each culture medium.

2.5. Spot test for initial confidence

The spot test is a primary corrosion inhibition test that shows the ability of corrosion inhibition of biopolymers. But, it is only a qualitative test and its results
are not proper to be used for comparison between biopolymers. Therefore, the biopolymers that did not show any corrosion signs on metal surface were qualified to furthermore accurate quantitative electrochemical studies. Spot test was performed by adding 1 mg ml\(^{-1}\) of each produced biopolymer to two different concentration corrosive solution, 35 mg ml\(^{-1}\) and 50 mg ml\(^{-1}\) NaCl solution [27]. A droplet of 50 μl of biopolymer- corrosive mixed solution was dropped on polished coupon surface and observed after 4 hr to compare with a droplet of corrosive solution without biopolymer as a control one.

2.6. Electrochemical studies

The electrochemical studies were carried out using carbon steel as work cell, saturated calomel and palatine electrodes, respectively as a reference and counter electrode.

The potentiodynamic polarization studies were performed by allowing the metal to attain steady state open circuit potential in 3.5% NaCl medium. It was then polarized in the positive direction starting at approximately 200 mV cathodic to \(E_{\text{corr}}\) and ending at approximately 200 mV anodic to \(E_{\text{corr}}\) at a scan rate of \(1 \text{ mV.s}^{-1}\).

The EIS studies were performed by applying small amplitude of AC signal of 10 mV at the OCP with a frequency range from 10 mHz to 100kHz. The analysis of impedance data was done by using Nyquist plot with value of the real part of the impedance, \(Z_{\text{re}}\) or \(Z'\) in x-axis and imaginary part of the impedance, \(Z_{\text{im}}\) or \(Z''\) in y-axis.

2.7. Fourier Transforms Infrared (FTIR) spectroscopy of biopolymers

Fourier Transforms Infrared (FTIR) spectra of the dried biopolymer were acquired by spectrophotometer (Spectrum RX I model, PerkinElmer, USA) in the frequency range of 4000–400 cm\(^{-1}\) using KBr pellet technique.

3. Results and discussion

3.1. Biopolymer production

The \(C.\ indologenes\) MUT.2 strain culture mediums with 5 constant ingredients (glutamic acid, \(K_2HPO_4\), \(NaH_2PO_4\), \(NH_4CL\) and \(MgSO_4\)) and different carbon sources were prepared for biopolymer production. Sucrose, glycerol as an experimental sources and molasses, cheese whey and corn steep liquor (CSL) as the low-cost industrial waste products were selected as the carbon sources. The amount of C element in the optimized culture medium was calculated by the molecular weight and density of sucrose. All the other carbon sources must supply this amount of C in their culture mediums. So, the required values of other carbon sources were calculated by their molecular weight and density. The produced biopolymers were accurately weighted and stored for further anti corrosion tests.
Table 1 indicates the required amounts of carbon sources and produced biopolymers.

**Table 1**

<table>
<thead>
<tr>
<th>Biopolymer name</th>
<th>Carbon source</th>
<th>Required carbon source (g L(^{-1}))</th>
<th>Biopolymer production (g L(^{-1}))</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bsuc</td>
<td>sucrose</td>
<td>21</td>
<td>17.6</td>
<td>0.13</td>
</tr>
<tr>
<td>Bgly</td>
<td>glycerol</td>
<td>22.6</td>
<td>15.7</td>
<td>0.36</td>
</tr>
<tr>
<td>Bmol</td>
<td>molasses</td>
<td>34.9</td>
<td>18.5</td>
<td>0.51</td>
</tr>
<tr>
<td>Bchw</td>
<td>cheese whey</td>
<td>25.7</td>
<td>17.2</td>
<td>0.26</td>
</tr>
<tr>
<td>BCSL</td>
<td>CSL</td>
<td>37.5</td>
<td>13.2</td>
<td>0.41</td>
</tr>
</tbody>
</table>

* In medium culture carbon sources were changed whereas other constituents were kept constant.

As can be seen in Table 1, the difference between the amounts of produced biopolymer in different culture medium is obvious. It shows the effect of changing the culture medium on the amount of produced biopolymer. In addition to the amounts of produced biopolymer, their color and visual quality varied in wide range from sticky-brown to completely white-powder.

### 3.2. Visual Spot test

The metal surface covered with corrosive-biopolymer droplets was observed frequently in a 4 hr time period. By comparing the inhibited solution droplets and the control one without biopolymer, it was obvious that all the biopolymers had inhibition ability. Fig 1 presents the metal surface covered with droplets of solution having biopolymer and control one without biopolymer inhibitor.

![3.5% and 5% NaCl corrosive solution](image)

Fig. 1 carbon steel coupon in contact with droplets of 3.5% and 5% NaCl corrosive solution and 1 g L\(^{-1}\) of: (0) control one without biopolymer, (1) Bsuc, (2) Bmol and (3) Bchw.

### 3.3. Electrochemical studies

**A. Tafel polarization measurement**

In corrosive solution, the corrosion process may be involved with anodic reaction; i.e. passage of metal ions from the metal surface into the solution and the
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cathodic reaction; i.e. evolution of hydrogen gas or the reduction of oxygen [28].
Fig 2 shows the Tafel polarization curves for the corrosion of carbon steel exposed to 3.5% NaCl solution in presence of 0.5g.L⁻¹ of different biopolymers. As it can be seen in Fig 2, the bacterial biopolymer can influence both the reaction of anodic and cathodic process by retarding metallic deterioration and also reducing the hydrogen evolution reaction [2].

![Tafel polarization plots of carbon steel in contact with 3.5% NaCl corrosive solution in the presence of different biopolymer inhibitors at 25 °C](image)

By adding the biopolymer inhibitor to aggressive medium the corrosion current density decreases while the corrosion potential partially move toward more negative values (except for B_mol biopolymer).

Different potentiodynamic parameters such as corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), cathodic Tafel slopes ($\beta_c$), anodic Tafel slopes ($\beta_a$) and corrosion rate (CR) values were obtained by Tafel polarization test. These data were tabulated in Table 2.

### Table 2

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>$E_{corr}$(mV/SCE)</th>
<th>$i_{corr}$(μA.cm⁻²)</th>
<th>$\beta_a$(mV/dec)</th>
<th>$\beta_c$(mV/dec)</th>
<th>CR (mm.y⁻¹)</th>
<th>LE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>-685</td>
<td>135</td>
<td>114</td>
<td>187</td>
<td>1.58</td>
<td>-</td>
</tr>
<tr>
<td>B_CSIL</td>
<td>-732</td>
<td>117.4</td>
<td>98</td>
<td>197</td>
<td>1.37</td>
<td>12.9</td>
</tr>
<tr>
<td>B_gly</td>
<td>-755</td>
<td>95.8</td>
<td>87</td>
<td>147</td>
<td>1.12</td>
<td>29</td>
</tr>
<tr>
<td>B_aac</td>
<td>-722</td>
<td>93.1</td>
<td>82</td>
<td>109</td>
<td>1.09</td>
<td>31</td>
</tr>
<tr>
<td>B_mol</td>
<td>-641</td>
<td>67.5</td>
<td>71</td>
<td>111</td>
<td>0.79</td>
<td>50</td>
</tr>
<tr>
<td>B_chw</td>
<td>-746</td>
<td>63.4</td>
<td>76</td>
<td>92</td>
<td>0.74</td>
<td>53</td>
</tr>
</tbody>
</table>

To compare the inhibition strength of different biopolymers, a parameter named Inhibition efficiency (I.E) was determined. The parameter can be calculated by $i_{corr}$ values as a following equation:
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\[ I.E.\, (\%) = \frac{i_{\text{corr}} - i_{\text{corr}}^*}{i_{\text{corr}}} \times 100 \]  

where \( i_{\text{corr}}^* \) and \( i_{\text{corr}} \) are respectively the corrosion current densities of inhibited and non-inhibited solution.

Biopolymer inhibitors can trap the corrosive metal ions in their cage-like structure. Some ions in the solution can catalyze the corrosion process; e.g. the Ferric (\( \text{Fe}^{3+} \)) ions can accelerate the formation of \( \text{Fe}^{2+} \) ferrous ions in carbon steel corrosion process and therefore, increasing the rate of corrosion [29]. Biopolymers can lower the corrosion process by blocking these ions in their structure. The biopolymer-ion complexes deposited on metal surface acts as a protective layer. This layer decreases the direct metal-corrosive medium contact and consequently lowers the rate of corrosion process. As can be seen in Table 2, the corrosion current density and corrosion rate decrease after adding biopolymers. Increasing the inhibition efficiency in the presence of biopolymers proves the inhibitive property of bacterial biopolymers.

If the difference between corrosion potential in solution with inhibitor and the solution without inhibitor exceeds ±85 mV, the inhibitor behaves separately as either anodic or cathodic inhibitor [30]. As can be observed from Table 2, here the displacement of corrosion potential is lesser than ±85 mV and therefor indicates that all biopolymers may act as a mixed inhibitor affect both anodic and cathodic reactions. The \( E_{\text{corr}} \) movement toward more negative values in the presence of inhibitor reflects that the biopolymers function more as cathodic inhibitor. The values of \( \beta_c \) and \( \beta_a \) do not change in a regular manner that proved the mixed mode of inhibition [31].

**B. Electrochemical Impedance Spectroscopy (EIS) measurements**

Impedance tests were carried out for carbon steel exposed to 3.5% NaCl solution in presence of different biopolymer inhibitors in medium temperature. Fig 3 is the three-element equivalent circuit which was used to simulate the impedance plots for carbon steel.

Fig. 3 Electrochemical Impedance Spectroscopy (EIS) best-fitted equivalent circuit diagram
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A one-time constant electrical fitted circuit proves that charge transfer process dominantly handles the electrochemical events [13]. The circuit consists of solution resistance (Rs), charge transfer resistance (Rct) and constant phase element of double layer CPE\textsubscript{dl}. CPE\textsubscript{dl} can be calculated by the value of Yo and n. Yo is the constant phase element (CPE) and n is a coefficient that can be used as a measure of surface homogeneity. The values of solution resistance (Rs) were nearly similar for different biopolymers. Results were tabulated in Table 3.

Table 3

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>R\textsubscript{ct} (Ω.cm\textsuperscript{2})</th>
<th>Yo (μΩ S/cm\textsuperscript{2})</th>
<th>n</th>
<th>C\textsubscript{dl} (μF.cm\textsuperscript{2})</th>
<th>I.E (％)</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>1321±11</td>
<td>349±8</td>
<td>0.51±0.02</td>
<td>154</td>
<td>-</td>
</tr>
<tr>
<td>B\textsubscript{CSL}</td>
<td>1532±23</td>
<td>302±12</td>
<td>0.52±0.03</td>
<td>148</td>
<td>13.7</td>
</tr>
<tr>
<td>B\textsubscript{gly}</td>
<td>1833±25</td>
<td>290±23</td>
<td>0.5±0.02</td>
<td>152</td>
<td>27.9</td>
</tr>
<tr>
<td>B\textsubscript{Suc}</td>
<td>1971±31</td>
<td>211±58</td>
<td>0.61±0.05</td>
<td>122</td>
<td>32.8</td>
</tr>
<tr>
<td>B\textsubscript{mol}</td>
<td>2687±18</td>
<td>183±34</td>
<td>0.57±0.03</td>
<td>107</td>
<td>51</td>
</tr>
<tr>
<td>B\textsubscript{chw}</td>
<td>2895±41</td>
<td>170±29</td>
<td>0.64±0.04</td>
<td>112</td>
<td>54.3</td>
</tr>
</tbody>
</table>

The values of charge transfer resistance were applied to calculate the values of double layer capacitance (C\textsubscript{dl}) and inhibition efficiency (I.E.).

\[
C_{dl} = (YoR_{ct}^{1-n})^{\frac{1}{n}} \tag{2}
\]

\[
I.E.(\%) = \frac{R_{ct}^* - R_{ct}}{R_{ct}} \times 100 \tag{3}
\]

where R\textsubscript{ct}\textsuperscript{*} and R\textsubscript{ct} are respectively the charge transfer resistance for solution in presence of biopolymers and solution in absence of biopolymers. The results of Tafel polarization method and electrochemical impedance method are in good agreement with one another. This confirms that rate of corrosion does not depend upon the measurement technique whereas the nature of inhibitor plays the main role [7].

The data in Table 3 demonstrate that addition of biopolymers to the corrosive solution increases the metal resistant property. The higher value of inhibition efficiency for B\textsubscript{chw} may be attributed to stronger layer formed on metal surface in this case. The decrease of C\textsubscript{dl} shows the thickening of electrical double layer and/or decrease of local dielectric constant. Typically, inhibitor adsorption on metal-solution interface reduce the electrical double layer resistance due to displacement of water molecules and other ions naturally adsorbed on the metal surface [5]. The higher homogeneity parameter (n) values in the presence of biopolymers reveals the decrease in roughness and inhomogeneity of surface [24].
Fig 4 represents the Nyquist, Bode modulus and Bode phase angle diagram of carbon steel in 3.5% NaCl solution in presence and absence of biopolymers.

In 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 x-axis...
is charge transfer resistance. As can be observed in Fig4 (a), the curves of Nyquist plots are not fully semicircle shape. This can be attributed to the inhomogeneity of the surface. In Fig4 (a), the greater amount of semicircles diameter is correspondent to higher amount of $Z'$ and consequently higher rate of corrosion resistance. Here, the greater semicircle diameter for $B_{chw}$ proves the higher rate of corrosion resistance for this biopolymer.

In Fig4 (b), the amounts of electrochemical impedance in low frequency range define as charge transfer resistance ($R_{ct}$). Results show higher values for solution with $B_{chw}$ and $B_{mol}$ biopolymers. Shift towards higher frequency reveals higher corrosion protection in Fig4(c) that is the other reason to priority of these two biopolymers.

4. The secret of anticorrosive property

4.1. Bacterial biopolymer recognition

FT-IR analysis was carried out to characterize the chemical structure and functional groups of the best inhibitor; i.e. $B_{chw}$ biopolymer. Biopolymers consist of macromolecules like proteins, polysaccharides, nucleic acids and lipids.

The inhibitive property of the biopolymers strongly depends on their ability to bind metal ions. Metal binding to biopolymers involves interaction between the metal ions and anionic functional groups of biopolymers (e.g. carboxyl, phosphate, sulfate, glycerate, pyruvate and succinate groups) that are common on the protein and carbohydrate constituents of biopolymers. The affinity of multi-dentate anionic ligands for multivalent ions, such as $Ca^{2+}$, $Cu^{2+}$, $Mg^{2+}$ and $Fe^{3+}$ can be very strong [32].

Fig 5 is the FTIR spectrum for $B_{chw}$ biopolymer. It was shown that the C. indologenes MUT.2 produced biopolymers are mainly comprised of polysaccharide [23]. Polysaccharides are mainly categorized as aldehyde or ketone. Here, the $-\text{C}=\text{O}$ carbonyl group stretching frequency at 1650-1750 cm$^{-1}$ can be a proof that biopolymer is mainly polysaccharide-based. This carbonyl group may be related to ketone and/or $-\text{C}=\text{O}$ stretching of COOH carboxylic acid group. The peaks around 1650-1750 cm$^{-1}$, 1370 cm$^{-1}$ and 1150 cm$^{-1}$ are respectively related to C=O stretching of COOH,COO$^-$ anti-symmetric stretching and C-O stretching of COOH [33]. The stretching bands at 900-1200 cm$^{-1}$ presents $-\text{C}=\text{O}$, that is the covalent bond connecting the monomer chains in saccharides [34]. $-\text{C}=\text{C}$- stretching band presents in 1600 cm$^{-1}$ and OH/NH groups band stretching is in 2900-3500 cm$^{-1}$ [35].
4.2. Corrosion inhibition mechanism

The inhibitive action of biopolymer inhibitor for carbon steel can be described in two general mechanisms: (1) the ferric ions (Fe$^{3+}$) formed as the result of oxidation of anodically produced Fe$^{2+}$ are trapped in biopolymer cage-like structure and the Fe$^{3+}$–biopolymer complex is precipitated on the metal surface. These deposits hinder the penetration of corrosive species such as oxygen or other metal ions to metal surface. In addition, up to catalytic effect of ferric ions on accelerating the corrosion process ($\text{Fe} + 2\text{Fe}^{3+} \rightarrow 3\text{Fe}^{2+}$), biopolymer lowers the corrosion rate by entraining these ions. (2) The ferrous ions (Fe$^{2+}$) trapped in the complexes act as a sacrificing anode in comparison to metal surface and survive the metal surface from corrosion [32].

The corrosion inhibition characteristics of the biopolymer can be related to their approach of adsorption on the metal surface. The adsorption mechanism depends on the nature of biopolymer interaction with metal surface which consequently causes a change in either mechanism of the electrochemical corrosion process or in the surface area available for the process. Therefore, criteria such as inhibitor physiochemical properties, the characteristics and surface charge of the metal, solution composition and pH are so effective [36].

The biopolymer adsorption on the metal surface is commonly categorized in two main approaches. The neutral molecules of the biopolymer components may be adsorbed on the metal surface by chemisorption mechanism involving the sharing of electrons between O or N atom and Fe and displacement of the water molecules from the metal surface.

\[
\text{Inhibitor}_{(\text{sol})} + xH_2O_{(\text{ads})} \rightarrow \text{Inhibitor}_{(\text{ads})} + xH_2O_{(\text{sol})}
\]

The protonated components of the inhibitor molecules may be physically adsorbed by the electrostatic interactions between the cations and adsorbed chloride ions. This is the probable adsorption mechanism of biopolymers on
carbon steel surface [5, 37]. The thermodynamic parameters declared physisorption of the biopolymers on the carbon steel surface.

Here in this work, the large protonated biopolymer competes with protons produced in hydrogen evolution and may be physically adsorbed on metal surface. The proton size is negligible compared to large compound biopolymer. Large biopolymer molecule covers almost all the metal surface and reduces both cathodic and anodic reactions by retarding the direct metal-solution contact. The obtained thermodynamic parameters for adsorption of this biopolymer on carbon steel surface prove the considered assertions. In addition, biopolymer having carbonyl groups can form a complex with metal ions and deposits on metal surface as a corrosion barrier layer [38]. The main factor in formation of biopolymer-iron complex is C=O stretching in ketone or carboxylic acid form [39]. The Fe ions are chelated or coupled with the carboxylic acid groups and the dipole-dipole interaction takes place in the metal/solution [39, 40].

5. Conclusion

The investigation results showed that the C. indologenes MUT.2 bacterial biopolymer can act as an ecofriendly green inhibitor for the corrosion control of carbon steel in 3.5% NaCl solution. Inhibition efficiency of the produced biopolymers varied when the biopolymers producing culture mediums changed.

The biopolymer cultivated in culture medium with cheese whey as a carbon source; Bchw, showed higher inhibition property. The bchw biopolymer acts as a mixed inhibitor affecting both anodic/cathodic reactions. The inhibitive action of the bchw biopolymer decreases the corrosion rate more than 2 times. This characteristic may be related to large biopolymer molecules participating in physical adsorption on metal surface.

Acknowledgment

The authors are so thankful to Malek Ashtar University of Technology for support of this article.

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