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Improvement of Pitting Corrosion Resistance in Type 201 Stainless Steel by Electrochemical Method in Nitric Acid Solution

Sri Hastuty [1,*], Fayza Yulia [1], Nonni Soraya Sambudi [2], Alfian Kahfi Fauzi [1],
Fatwa Khoirrun Nadhor [1]

[1] Department of Mechanical Engineering, Universitas Pertamina, Kota Jakarta Selatan, Daerah Khusus Ibukota Jakarta 12220, Indonesia
[2] Department of Chemical Engineering, Universitas Pertamina, Kota Jakarta Selatan, Daerah Khusus Ibukota Jakarta 12220, Indonesia

* Corresponding author: sri.hastuty@universitaspertamina.ac.id

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Abstract

Stainless steel is widely utilized across industries due to its robust resistance to corrosion. Stainless Steel 201 (SS201), characterized by a lower nickel content compared to grade 304, is valued for its cost-effectiveness and strong mechanical properties. However, SS201 is more prone to pitting corrosion in aggressive environments than SS304. This research aims to enhance SS201's resistance to pitting corrosion through surface treatment involving nitric acid. Cyclic voltammetry was conducted using nitric acid concentrations of 1, 2, and 3 M. The findings indicate that higher concentrations of nitric acid improved corrosion resistance, with 3 M resulting in a pitting depth of 23.667 µm. The application of citric acid contributed to enhanced resistance against pitting corrosion by fostering a chromium-rich surface.

1. Introduction

Stainless steel is widely used in a variety of industrial applications, such as pipes and storage tanks, due to its good mechanical properties and resistance to corrosion. However, stainless steel is not completely resistant to corrosion, and its corrosion resistance depends on the composition of the alloy and environmental conditions. Type 201 stainless steel is a cheaper alternative to type 304 stainless steel and is commonly used in the manufacture of cookware and automotive appliances [1, 2, 3].

Stainless steel is now widely used in industry along with new alloy variants. This material has excellent general corrosion resistance in a variety of environments. However, stainless steel also has a weakness in corrosion resistance to hole corrosion. Corrosion is a phenomenon of degradation of metal materials due to electrochemical reactions with the environment in which the material is placed. Electrochemical reactions consist of an anode, a cathode, and an electrolyte solution. The three metal components have a corrosive effect on the material. Since material loss due to corrosion leads to high production and maintenance costs, further attention should be paid to the factors that cause corrosion [4, 5, 6].

This corrosion may be caused by either the material itself or environmental factors. Material-related factors include purity, structural composition, and the presence of foreign elements. Environmental factors encompass air pollution levels, temperature, humidity, and the presence of corrosive substances, such as acids, bases, and salts, in both inorganic and organic forms [7, 8, 9].

To achieve high oxidation resistance, chromium is typically added in amounts ranging from 13% to 26%. This promotes the formation of a passive chromium(III) oxide (Cr_2O_3) layer, which is extremely thin and invisible, ensuring it does not affect the appearance of the stainless steel. Due to its resistance to water and air, stainless steel does not require additional protective coatings, as this passive layer rapidly regenerates when scratched. Strong oxidizing conditions favor the formation of this layer, which is why the process is referred to as "passivation" [10, 11, 12]. The passive film forms spontaneously when stainless steel comes into contact with air or oxygen-containing electrolytes, and surface treatment with HNO_3 solution aims to enhance this protective passive layer [10].

This study aims to determine the effect of surface treatment in nitric acid on the corrosion resistance of type

201 stainless steel (SS201), as well as to optimize potentiodynamic polarization parameters such as scan rate, potential range, and electrolyte concentration to enhance the material's performance. Additionally, it seeks to understand the corrosion inhibition mechanism and the impact of polarization techniques on the microstructure of SS201. Introducing a novel approach, this research employs cyclic voltammetry (CV) with nitric acid as a surface treatment method, offering more controlled and uniform passive layer formation through electrochemical cycling.

Unlike previous studies that focused primarily on potential dynamic and immersion methods—such as the work by Hastuty *et al.* [10] and the use of citric acid immersion reported by Sugawara *et al.* [13]—this study provides a comparative analysis between CV and traditional immersion methods, highlighting the advantages and limitations of each technique. The focus on SS201 adds to the novelty, as most prior studies have concentrated on other stainless steel grades, despite SS201's growing industrial relevance due to its cost-effectiveness and availability. Overall, this study aims to provide insight into the corrosion behavior of SS201 in nitric acid environments and to develop an effective corrosion resistance strategy using potentiodynamic polarization, with potential applications in various industrial fields.

2. Experimental

The methodology of this research involves applying surface treatment to SS201 using cyclic voltammetry in nitric acid solutions with varying concentrations of 1, 2, and 3 M. Corrosion testing was conducted in a 3.5 wt% sodium chloride (NaCl) solution.

2.1. Materials

The material used in this research was Stainless Steel 201 (SS201), which was cut into specimens measuring 30 × 30 × 5 mm. A 65% HNO_3 solution was used to prepare nitric acid solutions with concentrations of 1, 2, and 3 M for surface treatment. Corrosion testing was performed using a 3.5 wt% NaCl solution. All electrochemical measurements, including cyclic voltammetry and corrosion testing, were conducted using an Autolab GSTAT 302N.

2.2. Experiment

Surface treatment was carried out using two methods: cyclic voltammetry and immersion. The cyclic voltammetry method involved immersing the SS201 samples for 60 minutes with 50 scan cycles, as illustrated in Figure 1. The immersion method also involved a 60-minute treatment in nitric acid without electrochemical cycling. Following surface treatment, the samples were analyzed using an optical microscope and SEM-EDS to observe surface morphology and elemental distribution. Corrosion testing was then performed using open-circuit potential (OCP) and anodic polarization techniques. After the corrosion tests, the sample surfaces were re-examined with a microscope to evaluate the diameter and depth of pitting corrosion that developed on the SS201 surface.

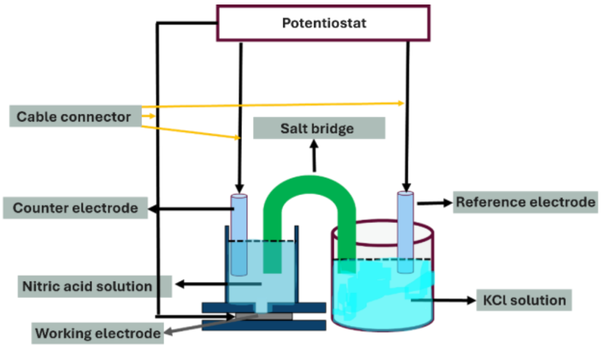


Figure 1. Schematic of surface treatment process

3. Results and Discussion

3.1. Surface Treatment

Before conducting corrosion testing using the OCP method and anodic polarization (Tafel), the test specimens underwent surface treatment through immersion and cyclic voltammetry methods for 60 minutes. This treatment aimed to enhance the corrosion resistance of SS201. Nitric acid solutions with concentrations of 1 M, 2 M, and 3 M were selected for surface treatment due to their effectiveness in promoting the formation of protective passive films that improve pitting corrosion resistance without causing surface damage [10].

The results of surface treatment with these concentrations are presented in Table 1, where a significant increase in current density was observed during the first CV scan. This increase is attributed to the formation of passive films and the anodic dissolution of constituent metals. In subsequent scans, the current density gradually decreased, indicating stabilization of the passive layer, with consistent reduction observed up to the 50th scan. As shown in Figure 2, the current density at 0.9 V was highest for the 3 M nitric acid treatment across all scans, compared to the 1 M and 2 M treatments.

Table 1. Results of surface treatment using nitric acid

Scan	Cyclic voltammetry 1 M HNO_3 (i/A cm^{-2})	Cyclic voltammetry 2 M HNO_3 (i/A cm^{-2})	Cyclic voltammetry 3 M HNO_3 (i/A cm^{-2})
1	9.93039×10^{-5}	1.09774×10^{-4}	1.1348×10^{-4}
2	3.22411×10^{-5}	3.6644×10^{-5}	3.70232×10^{-5}
3	2.14771×10^{-5}	2.38427×10^{-5}	2.3871×10^{-5}
4	1.66553×10^{-5}	1.81041×10^{-5}	1.81268×10^{-5}
5	1.34975×10^{-5}	1.49774×10^{-5}	1.54329×10^{-5}
10	7.86078×10^{-6}	8.46633×10^{-6}	2.75608×10^{-6}
20	2.7674×10^{-6}	2.91171×10^{-6}	2.99943×10^{-7}
30	2.12224×10^{-6}	2.21279×10^{-6}	2.20713×10^{-7}
40	1.78268×10^{-6}	1.66101×10^{-6}	1.41483×10^{-7}
50	2.88625×10^{-7}	1.89587×10^{-7}	1.01868×10^{-7}

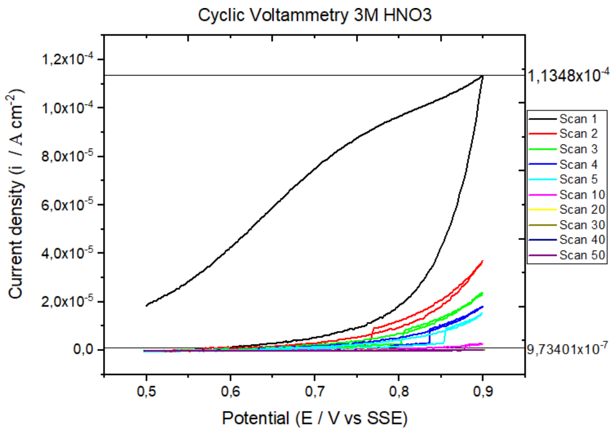


Figure 2. Cyclic voltammetry using 3 M nitric acid

3.2. Corrosion Testing

3.2.1. Open Circuit Potential (OCP)

The open circuit potential (OCP) test was conducted before the corrosion test to assess the interaction between the corrosive solution and the specimen surface, and to evaluate electrochemical stability. During the test, the potential of each specimen was measured under stable conditions without any current flow. The results, plotted as potential vs. time, reflected the electrochemical stability of the treated surfaces.

The results of the OCP test showed variations in potential values across different concentrations. The highest stable potential (0.15507 V) was observed in the SS201 specimen treated with 3 M nitric acid using cyclic voltammetry, while the lowest (-0.17046 V) was recorded in the untreated specimen.

As shown in Figure 3, all specimens exhibited fluctuating OCP curves. SS201 specimens, both treated and untreated, showed more instability in NaCl solution due to chloride ions damaging the passive layer and accelerating surface degradation. This was consistent with the pitting analysis, which indicated more severe damage in untreated specimens. The surface damage caused by NaCl created irregularities and gaps, making the specimen surfaces uneven. As a result, the system required more time to reach electrochemical stability before corrosion testing. This instability contributed to the fluctuating behavior observed in the OCP graphs.

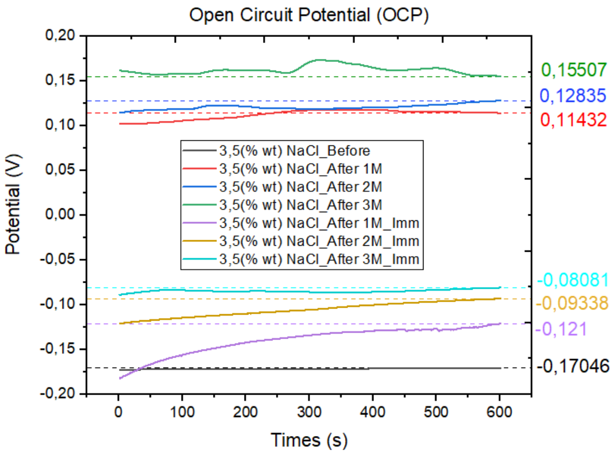


Figure 3. OCP results from SS201 using nitric acid

3.2.2. Anodic Polarization

Following the OCP test, corrosion testing was conducted using the anodic polarization Tafel method with an Autolab potentiostat to obtain Tafel plots, from which the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) values were determined. The experiment was performed in a 3.5 wt% NaCl solution. The linear sweep voltammetry (LSV) curves, shown in Figure 4, illustrate the results of the anodic polarization test. In the NaCl solution, E_{corr} values varied depending on the surface treatment applied. Untreated specimens exhibited an E_{corr} of -0.51019 V, while specimens treated by immersion in 3 M nitric acid showed an improved E_{corr} of -0.29032 V. These results indicate that increasing the concentration of the surface treatment enhances the corrosion resistance of SS201 in the corrosive NaCl environment. The I_{corr} values were obtained by analyzing each Tafel curve using Origin software. The observed fractures correspond to the formation of a new passive film in the second active anodic region, which results from chemical passivation reactions in the nitric acid solution.

The anodic polarization Tafel test generates forward and reverse curves, which are used to determine the pitting potential ($E_{pitting}$) and repassivation potential ($E_{repassivation}$). $E_{pitting}$ is the potential at which pitting corrosion begins on the specimen surface due to NaCl exposure, while $E_{repassivation}$ is the potential at which the surface starts to heal or repassivate after the damage. The difference between $E_{pitting}$ and $E_{repassivation}$ indicates the potential range needed for recovery, reflecting the surface's ability to repair itself after corrosion.

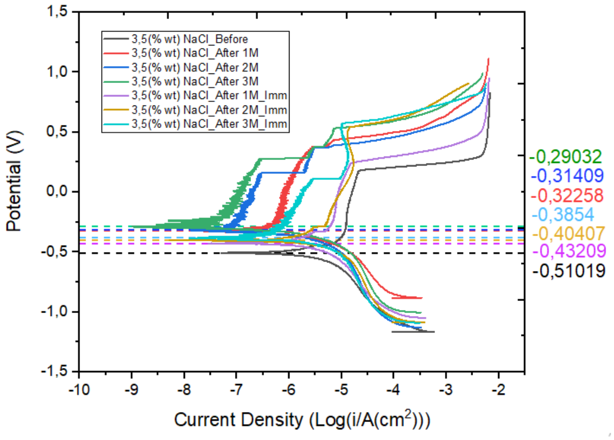


Figure 4. The polarization curve of SS201 after nitric acid surface treatment

Table 2. E_{corr} of SS201 using nitric acid

Surface treatment	E_{corr} (V)
Before treatment	-0.51019
1 M immersion	-0.43209
2 M immersion	-0.40407
3 M immersion	-0.3854
1 M cyclic voltammetry	-0.32258
2 M cyclic voltammetry	-0.31409
3 M cyclic voltammetry	-0.29032

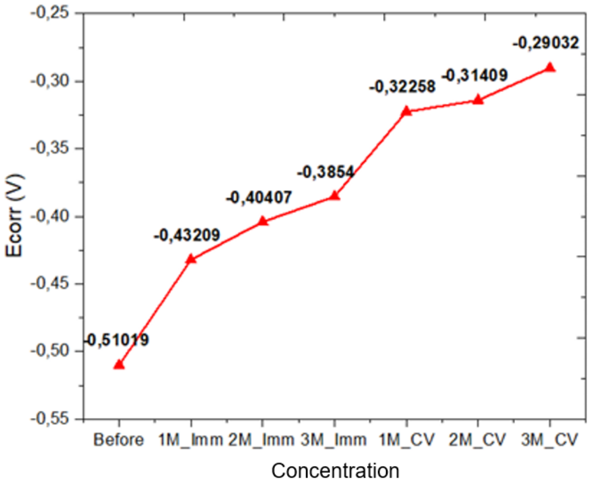


Figure 5. The E_{corr} for immersion and cyclic voltammetry surface treatment

Figure 5 and Table 2 compare the E_{corr} of SS201 in a 3.5 wt% NaCl solution under different surface treatments. The untreated specimen exhibits the most negative E_{corr} value (-0.51019 V), indicating high corrosion susceptibility. In contrast, specimens treated via immersion and cyclic voltammetry exhibit a positive shift in E_{corr}, suggesting improved corrosion resistance. This trend becomes more pronounced with increasing nitric acid concentrations from 1 M to 3 M, especially in immersion-treated samples, which show more consistent improvement. The shift toward less negative potentials indicates the formation of a protective passive layer that limits anodic dissolution. The 3 M immersion treatment achieves the most favorable E_{corr}, demonstrating the highest effectiveness among all conditions tested.

As shown in Figure 6, the forward and reverse Tafel polarization curves in 3.5 wt% NaCl after 3 M immersion reveal a clear passive region during the forward scan. This forward curve is then followed by a sharp current increase at higher potentials, suggesting passive film breakdown. The non-overlapping curves between the forward and reverse scans further confirm irreversible pitting behavior, highlighting the aggressive role of chloride ions in disrupting passivity.

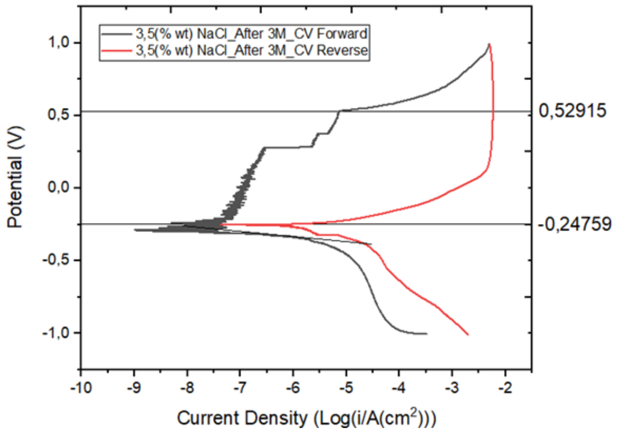


Figure 6. Forward and reverse Tafel polarization curves

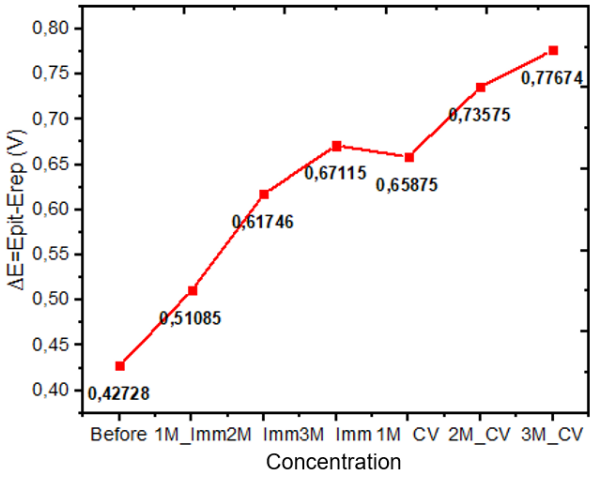


Figure 7. $E_{pitting}$ and $E_{repassivation}$ curve

Analysis of the $E_{pitting}$ and $E_{repassivation}$ further supports these findings. The highest $E_{pitting}$ value, 0.57612 V, was observed in the specimen treated by 3 M immersion, indicating strong resistance to pitting corrosion initiation. The highest $E_{repassivation}$ value, -0.1748 V, was found in the 2 M treated specimen, reflecting effective surface recovery. Conversely, the lowest $E_{pitting}$ value, 0.17445 V, occurred in the untreated specimen, and the lowest $E_{repassivation}$ value, -0.25396 V, was observed in the 1 M immersion specimen. The potential difference (ΔE) between $E_{pitting}$ and $E_{repassivation}$ in Figure 7 reflects the recovery time required after pitting corrosion occurs.

3.3. Microscopic Visual

Macrostructure and microstructure analyses, summarized in Tables 3 and 4, reveal distinct areas affected by pitting corrosion in SS201. A clear difference is observed between specimens with and without surface treatment. In the 3.5 wt% NaCl solution, pitting holes are prominently visible. While all specimens exhibited pitting corrosion, those without surface treatment showed significantly larger and more numerous pits compared to treated samples. Corrosion testing using the anodic polarization Tafel method further supports these findings, demonstrating that untreated specimens exhibit the lowest E_{corr} values, indicating greater susceptibility to corrosion.

Corrosion testing of SS201 using the anodic polarization Tafel method revealed the occurrence of pitting corrosion. This phenomenon was further analyzed for each test specimen by assessing the number of pits, pit depth, and pit diameter. ImageJ software was used to quantify these parameters for specimens both with and without surface treatment.

The results of pitting corrosion analysis using the ImageJ application are presented in Table 5. In the 3.5 wt% NaCl corrosive solution, the untreated specimen exhibited a total of 85 pits with an average diameter of 182.22 µm. In contrast, the specimen treated with 3 M cyclic voltammetry showed a significant reduction in the number of pits to 19, but with an increased average diameter of 488.24 µm. This indicates a notable difference in both the number and size of pits depending on the treatment method and concentration.

Table 3. Macroscopic visuals

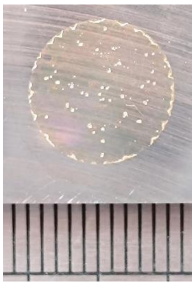
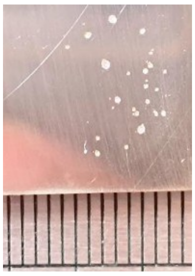
Examination	1 M	2 M	3 M
Immersion			
Cyclic voltammetry			
Without surface treatment			

Table 4. Microscopic visuals

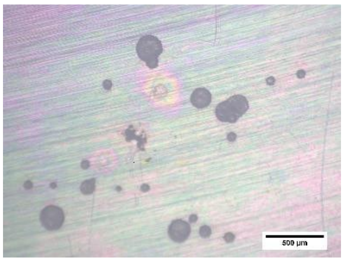
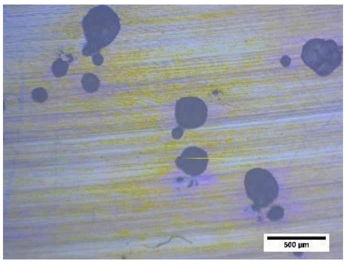
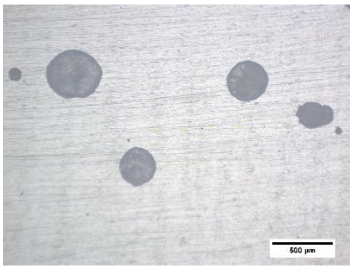
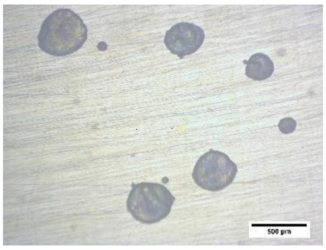
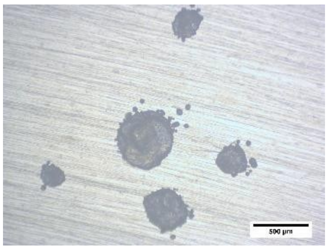
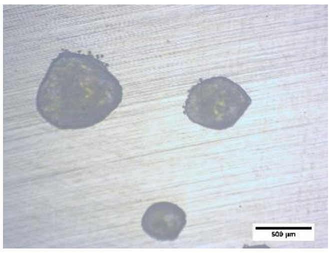
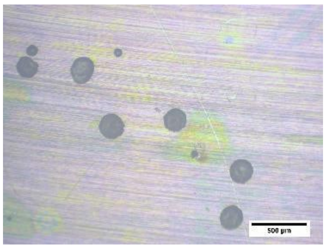
	1 M	2 M	3 M
Immersion	 	 	
Cyclic voltammetry	 	 	
Without surface treatment		 	

Table 5. Diameter and depth of pitting

Concentration	Number of pitting	Average diameter of pitting (µm)	Average depth (µm)
Before treatment	85	182.22	50.42
1 M immersion	62	187.63	44.25
2 M immersion	58	214.27	42.19
3 M immersion	51	285.45	40.13
1 M cyclic voltammetry	34	312.77	36.02
2 M cyclic voltammetry	28	417.54	28.81
3 M cyclic voltammetry	19	488.24	23.67

Additionally, the average pit depth decreased substantially from 50.42 µm in the untreated specimen to 23.67 µm in the 3 M cyclic voltammetry-treated specimen, representing a reduction of approximately 53%. These results demonstrate that surface treatment with nitric acid, especially using cyclic voltammetry, effectively reduces the depth of pitting corrosion and alters the pit morphology, contributing to improved corrosion resistance. This suggests that surface modification not only mitigates the initiation of new pits but also limits the extent of pit propagation.

3.4. SEM and EDS Analysis

SEM-EDS analysis revealed notable differences in the surface morphology and elemental composition of SS201 before and after nitric acid surface treatment, as shown in Figure 8. Prior to treatment, the surface was relatively uniform with no significant topographical damage. Elements such as Fe, O, Ni, Cr, and Cl were evenly distributed, indicating a homogeneous passive layer without evident localized corrosion.

After treatment with nitric acid, pitting corrosion was still present but significantly reduced in both severity and density compared to untreated specimens. As seen in Figure 9, SEM-EDS results showed that Fe, O, Ni, Cr, and Cl remained detectable, particularly in the pitted regions. The enrichment of Ni and Cr in these areas is important, as these elements promote the formation and stabilization of protective passive films, enhancing corrosion resistance. The presence of compounds such as FeCl, NiO, Cr_2O_3, and ferric hydroxides suggests that chemical reactions between nitric acid and the stainless steel surface contributed to the development of oxide and hydroxide layers. These layers act as barriers against chloride attack, lowering surface reactivity and inhibiting the progression of pitting corrosion.

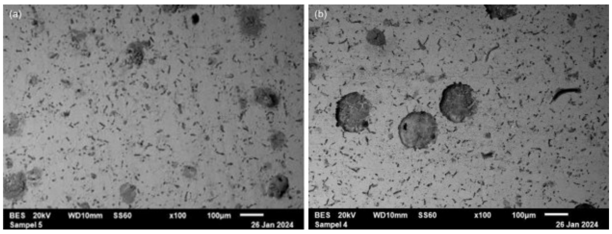


Figure 8. SEM images of the SS201 surface: (a) before surface treatment and (b) after surface treatment with nitric acid

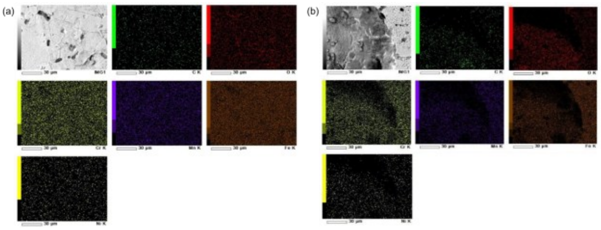


Figure 9. EDS images of SS201 surface: (a) before and (b) after surface treatment

Chromium plays a key role in forming the Cr_2O_3 film, while nickel improves the alloy's resistance in acidic and chloride-rich environments, resulting in a more corrosion-resistant surface. Although some pitting corrosion remains, nitric acid surface treatment clearly inhibits its development. The treated surface exhibits enhanced resistance to chloride-induced damage, demonstrating the effectiveness of nitric acid in modifying surface chemistry to favor passivation. Thus, while corrosion is not completely eliminated, it is substantially mitigated, producing a more stable and less damaged surface.

4. Conclusion

This study concludes that surface treatment through immersion and cyclic voltammetry in nitric acid enhances the corrosion resistance of stainless steel 201 by promoting the formation of a protective chromium oxide (Cr_2O_3) passive layer. Increasing the nitric acid concentration from 1 M to 3 M significantly reduces pitting depth by up to 53.06% at 3 M using cyclic voltammetry—and decreases the number of pits from 85 (untreated) to 19 (treated), indicating a notable improvement in resistance to pitting corrosion.

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