Research   JoPC

The Effect of Dried Green Alga *Chlorella sorokiniana* MH923013 on Corrosion Protection of Stainless Steel in Saline Media

Noor Ali Khudhair[1],*, Ibrahim J. A Bed[2], Shahla O.F. Alogaidi[3], Roaa A. Abd Alrhman[4]

Abstract.
Metals interact with their surroundings to undergo corrosion, which is also defined as surface damage or metal decline in an aggressive setting. The objective of the current study was to assess the ability of the green alga Chlorella sorokiniana MH923013 to prevent corrosion of stainless steel in saline medium. Atomic force macroscopy (AFM) and Fourier transform infrared spectroscopy (FT-IR) were used to analyse a dry mass of green algae. Electrochemical polarization technique was used to test the corrosion of stainless steel (S.S.) in saline solution (blank) and inhibitor (green algae) solutions in various concentrations at temperatures ranging from 298 to 318 K. The kinetic and thermodynamic activation parameters (Ea, H, S, and G) for blank and inhibitor solutions were determined.

Keywords: Stainless steel, green algae, chloride, corrosion, electrochemical polarization technique

INTRODUCTION

Corrosion is an unavoidable part of life. Corrosion is a chemical or electrochemical interaction that occurs between a material, usually a metal, and its environment, resulting in the deteriotation of the material's deteriorating. Stainless alloy is one of the most used materials. It has excellent mechanical properties and low costs compared with other metals and wide availability, so stainless steel is a popular material. Corrosion inhibitors are commonly used to decrease the unwanted base metal dissolving caused by these processes. To preserve metallic components from corrosion, the hunt for new and effective corrosion inhibitors, particularly in saline solutions, has become a necessity [1–3].

*Author for Correspondence
Noor Ali Khudhair
E-mail: noor.ali.khudair@gau.edu.iq

[1]Lecturer, Medical Laboratories Techniques Department, College of Medical and Health Technologies, Gilgamesh Ahliya University Baghdad, Iraq
[2]Lecturer, Department of Biology, College of science, University of Baghdad, Baghdad-Al-Jadiria, Iraq
[3]Lecturer, Medical Laboratories Techniques Department, College of Medical and Health Technologies, Gilgamesh Ahliya University Baghdad, Iraq
[4]Lecturer, Radiology and Sonar Department, College of Medical and Health Technologies, Gilgamesh

Designing chemicals, commercial products, and chemical technologies with the intention of avoiding toxins and reducing waste has become very attractive in the previous 10 years. There was already an increase in concern about waste production and the usage of poisonous and dangerous substances in the 1980s [4]. Bio corrosion is a difficult and poorly understood process [5].

Metals transmit electrons to their surroundings through chemical or electrochemical oxidation processes, changing their valence from zero to a positive value. The surroundings include gas, liquid, and soil-liquid hybrids. These conditions, known as electrolytes, have conductivity for the transfer of electrons [6]. A corrosion inhibitor is a chemical substance that is adsorbed on a metal or

alloy surface to form a protective film, shielding the alloy's surface from environmental reactions or reducing the amount of ions that attack the metal's surface [7]. Most effective corrosion inhibitors are heteroatom-containing compounds with oxygen, sulfur, or nitrogen atoms in their structures. Bio corrosion is a complicated and poorly understood component and many studies have discussed the effect of live algae and their bloom on corrosion, because of the conflicting results regarding live algae and their impact on increasing or decreasing corrosion [8, 9]. Little attention has been paid to focus on the dry mass of algae and its ability to prevent corrosion. Experiments were conducted to investigate how the dry mass of the green alga *Chlorella sorokiniana* MH923013 might affect corrosion. The composition and chemical properties of the film formed on the alloy determine how effectively algae are inhibited. Because of how well green algae prevent corrosion, those that contain nitrogen have frequently been used [6, 10]. These compounds were chosen because they (a) have extraordinarily high molecular weights, (b) have broad connections in the form of aromatic rings, and (c) have functional polar groups (such as -C=O and C=N).

MATERIAL AND METHODS

The experiment was created to examine the impact on corrosion by exposing steel pieces to various concentrations of the dried green alga, Selected parameters were recorded and analyzed. The mass of steel pieces were the parameters.

Steel Specimen Preparation

In the beginning, concentrated HCl (37%, Fluka/Switzerland) was used to pickle the steel rebar, washed with tap water, then rinsed with ethanol, and dried completely. Then the rebar was attached with adhesive tape, and an area of it was left exposed, which is 16.55 cm^2, and placed in a three-electrode cell with the Pt electrode serving as counter electrode and the Ag/AgCl electrode serving as the reference electrode.

Surface Profile
#### *Corrosion Measurement and Data Recorded*

The potentiostat set up include (thermostat, host computer, magnetic stirrer, galvanostat, potentiostat, and Mat lab Germany 2000). The Pyrex cell has a capacity of 1 L and includes interior and external bowls. The electrochemical corrosion cell consists of three electrodes. Stainless steel is utilized as the working electrode to calculate its potential in relation to the reference electrode, with platinum with length 10 cm serving as the auxiliary electrode and silver-silver chloride (Ag/AgCl, 3.0 M KCl) as the reference electrode. To create steady state open circuit potential (E_{ocp}), the working electrode was dipped in the test solution for 15 minutes. Then, in a potential range of 200 mV, electrochemical measurements were performed. All tests were done by using a cooling-heating circulating water bath to keep a temperature range of 298 to 318 K.
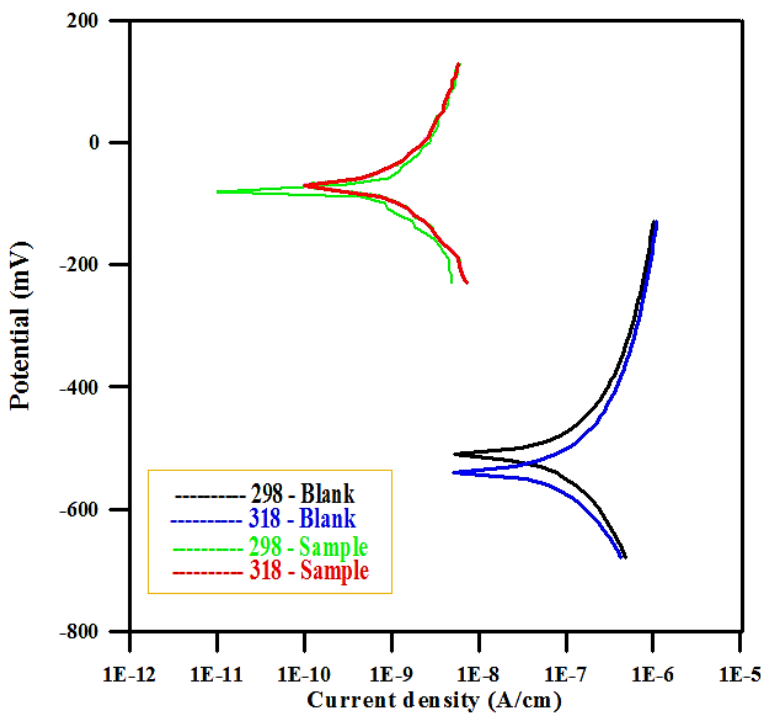
Polarization Curves

Table 1 and Figures 1, 2, and 3 show the results of the evaluation of the corrosion parameters. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were determined in the absence and presence of inhibitor molecules in NaCl solution by the extrapolation of the cathodic and anodic Tafel plots. From Figures 1, 2, and 3, the anodic (ba) and cathodic (bc) Tafel slopes were also determined. The corrosion current density (icorr A/cm^2), corrosion potential (Ecorr mV), cathodic and anodic Tafel slopes (bc) and (ba) (mV/Dec), weight loss (WL) (g/m^2.d), penetration loss (PL) (mm/y), and protection efficiency (PE%) are shown in Table 1. The Tafel diagram reveals that in the presence of inhibitors the (E_{corr}) for stainless steel shifts to a high (noble) level compared to the blank solution, and this indicates that the protection is anodic protection. Tafel plot data suggests that the protection functions as an anodic protection because Ecorr for stainless steel in the presence of the inhibitors shifts to a higher (noble) position in comparison to blank solution. The following equation was used to calculate the inhibition efficiency (%IE) [10, 11]:

$$\%IE = \frac{(icorr)o - (icorr)}{(icorr)o} * 100 \tag{1}$$

where $(i_{corr})_o$ is the corrosion current density when no inhibitors are present, (i_{corr}) is the corrosion current density when there are inhibitors present. Green algae showed good inhibition efficiencies. This is because they contain carbonyl, imide groups, contain heterogeneous rings, also contain oxygen, nitrogen which form with metal a complex that adsorb on the surface of alloy and protect it from corrosive media [11, 12].
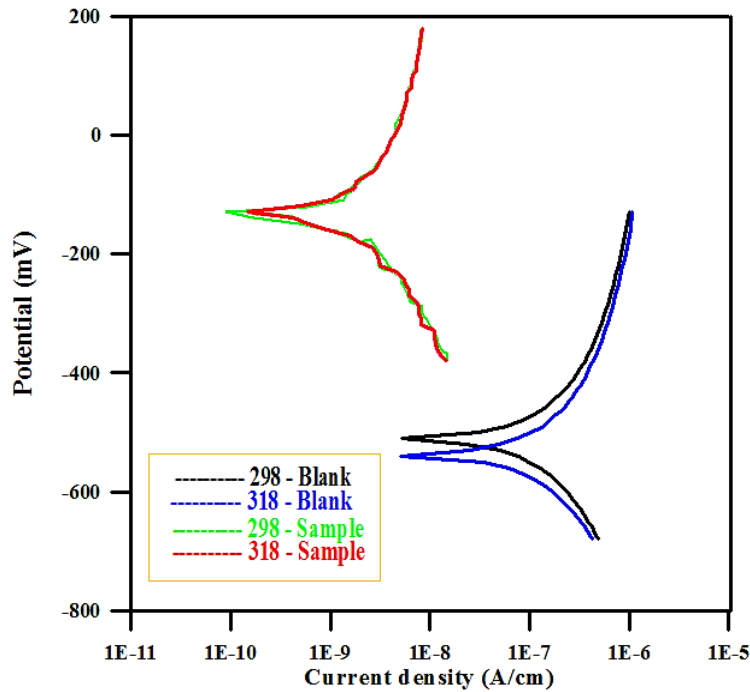
Figure 1. Polarization curves for corrosion of blanks and with 0.05 mg green algae in a solution of 3.5% NaCl at different temperatures.

Figure 2. Polarization curves for corrosion of blanks and with 0.1 mg green algae in a solution of 3.5% NaCl at different temperatures.
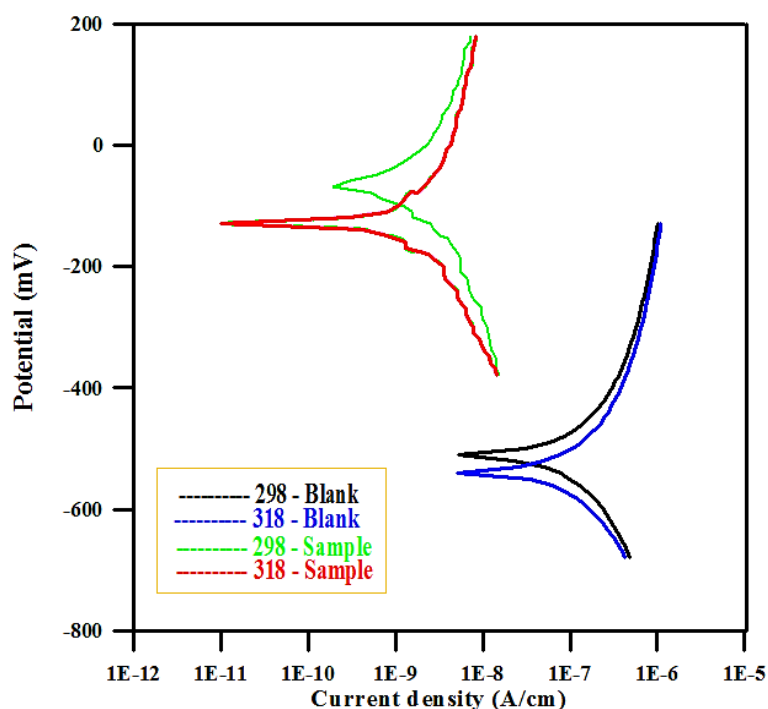
Figure 3. Polarization curves for corrosion of blanks and with 0.5 mg green algae in a solution of 3.5% NaCl at different temperatures.

Table 1. Corrosion parameters for blank solutions and inhibitors solutions at temperature range (298–318 K)

Comp.	Temp	-E$_{corr}$ (mV)	i$_{corr}$ (µA/cm²)	-Bc (mV/Dec)	Ba (mV/Dec)	WL (g/m².d)	PL (mm/y)	IE%
Blank	298	-510.1	94.58	-224.8	217.2	23.6	1.10	-
	318	-538.9	102.95	-224.3	234.6	25.7	1.19	-
0.05 mg green algae	298	-133.6	1.77	-248.4	373.3	0.444	0.0206	98
	318	-132.8	2.68	-349.1	566.8	0.670	0.0311	97
0.1 mg green algae	298	-81.1	1.58	-264.4	334.9	0. 395	0.0184	98
	318	-71.0	1.91	-295.3	410.7	0.478	0.0222	98
0.5 mg green algae	298	-66.9	0.835	-133.7	163.7	0.209	0.00970	99
	318	-128.3	1.32	-207.9	247.5	0.331	0.0154	99

Kinetic and Thermodynamic Activation Parameters

Thermodynamic activation parameters, including the activation energy (Ea∗), enthalpy of activation (ΔH∗), and entropy of activation (ΔS∗) were calculated by using the Clausius–Clapeyron and Arrhenius equations which has an alternative formula known as the transition state [13, 14].

$$log \frac{Icorr.2}{Icorr.1} = \frac{\Delta H*}{2.303R} + \frac{(T2-T1)}{T2T1} \tag{2}$$

where Icorr is the corrosion rate, ΔH∗ is the enthalpy of activation, Ea∗ is the activation energy), R is the gas constant equal to 8.315 JK⁻¹mol⁻¹), and T is the absolute temperature (K). The following equation represents the transition state:

$$\text{Log Icorr./T} = Log\left[\frac{R}{Nh} + \frac{\Delta S*}{2.303R}\right] - \frac{\Delta H*}{2.303RT} \tag{3}$$

where N is the Avagadro number (6.022 × 10²³ mol) and h is the Planck's constant (6.62 × 10⁻³⁴ J.S). The following equation was used to calculate entropy of activation (ΔS∗), enthalpy of activation (ΔH∗), and the free energy of activation (ΔG∗) [5]:

$$\Delta G* = \Delta H* - T\Delta S* \tag{4}$$

RESULTS AND DISCUSSION

There are many ways that live algae can affect corrosion. Algae have a direct, indirect, and disruptive impact on systems for preventing corrosion. Algae adjust their environment by affecting the pH and oxygen levels in the immediate area, as well as by creating metabolites that alter the electrolyte and generally make it more corrosive-friendly. Photosynthesizing algae can cause a pH increase to greater than 10 and a pH decrease to less than ambient saltwater throughout the decay process. In one instance, the authors discovered a dying culture's pH to be 1.8 [15].

In our study, the dry weight of green algae was selected to test the capability to work as inhibitor of corrosion.

The results indicate that the thermodynamic activation parameters Ea* and $\Delta H*$ were lower than the uninhibited one. The reason for this may be that at higher temperatures the coverage of the inhibitor molecules on the surface of the metal increases. This suggests that the rate at which the chemical absorbed layer forms may be faster than the rate at which it dissolves at high temperatures [16]. According to a different viewpoint, certain types of inhibitors in aqueous solutions change the corrosion reaction ways by suggesting alternative reaction pathways with lower activation energies [5]. This characteristic promotes the reduction of metal corrosion rate [4]. The negative inhibitory entropy $\Delta S*$ suggests a high degree of adsorption regularity during the activation phase, indicating the creation of the activated complex and a reduction in degrees of freedom. According to Table 2, the free energy activation showed positive values. The activated complex was not stable, and the likelihood of its creation reduced with increasing temperature, as indicated by the slight change that appears [11, 17].

**Table 2.** Kinetic and thermodynamic activation parameters.

Sample	T (K)	Ea* (kJ/mol)	$\Delta H*$ (kJ/mol)	$\Delta S*$(kJ/mol.K)	$\Delta G*$(kJ/mol)
Blank	298	0.158	0.158	-0.20713	61.883
	318				66.025
0.05 mg green algae	298	0.197	0.197	-0.24021	71.78
	318				76.584
0.1 mg green algae	298	0.1	0.1	-0.24115	71.963
	318				76.786
0.5 mg green algae	298	0.125	0.125	-0.24646	73.57
	318				78.499

When the inhibitors are present, the Ecorr of the stainless steel changes to a higher value compared to blank sample, suggesting that the inhibitors serve as anodic protection. Inhibition efficiency (IE%) was decreased with increasing temperature for all solutions that form with metal a complex that adsorb on the surface of alloy and protect it from corrosive media [18–20].

Figure 4 is a three-dimensional figure of the surface of green algae with the atomic force device. Figure 4A is before using green algae and Figure 4B is after using green algae as additive, which seems to be unaffected and more softened with the average size equal to 26 and 54 nm for surface before and after using green algae, respectively.

Figure 5 and 6 show the surface roughness (before and after using green alga) These images clearly support the investigations deduced from the electrochemical polarization procedure, since the surface morphology in 3.5% NaCl without using green algae is very rough containing deep valleys (Figure 4A).
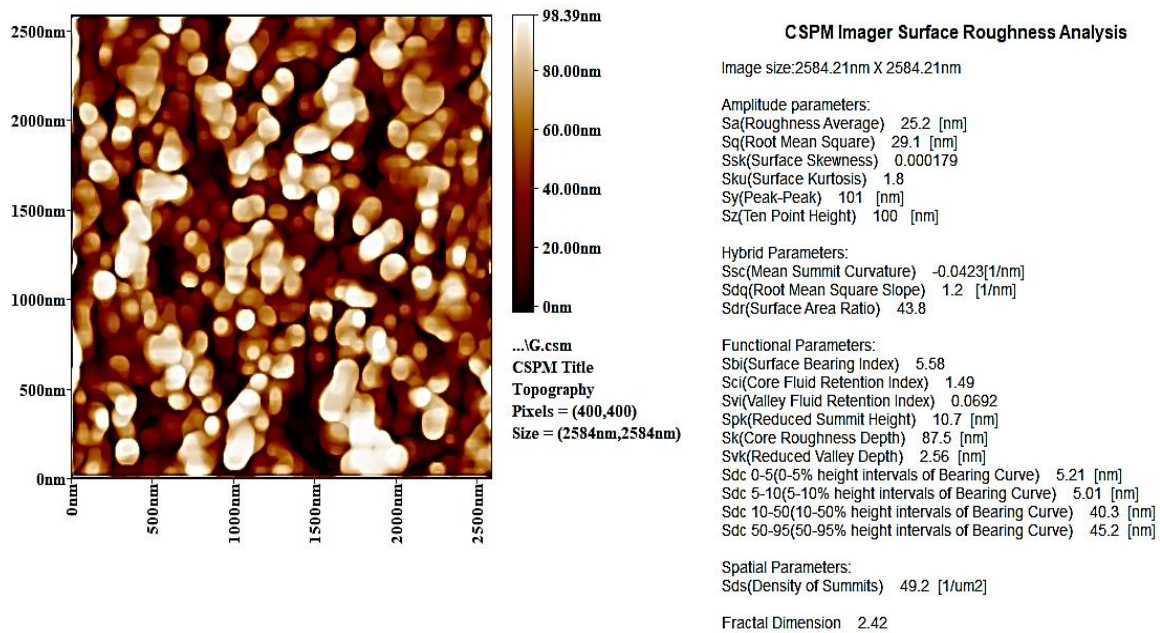
These images prove the results obtained by electrochemical polarization procedure, because at
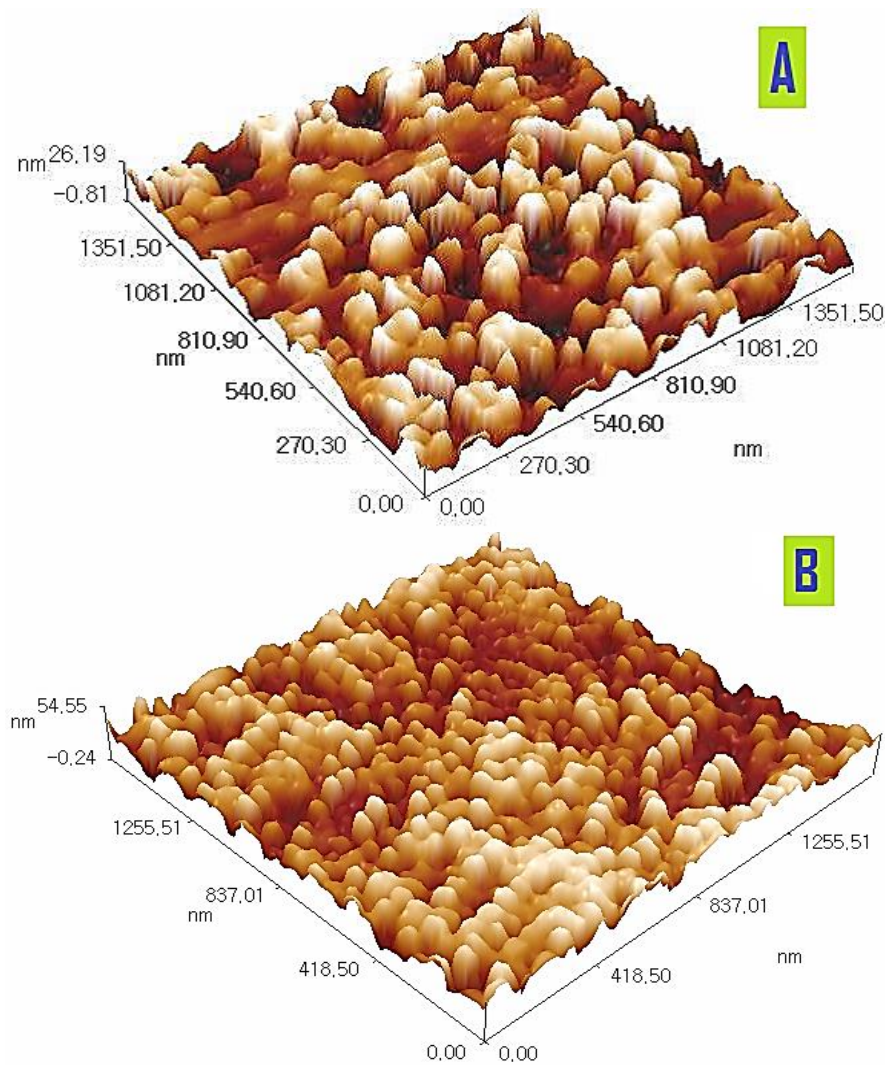
Figure 4. Three-dimensional image (A) before using green algae and (B) after using green algae as additive.
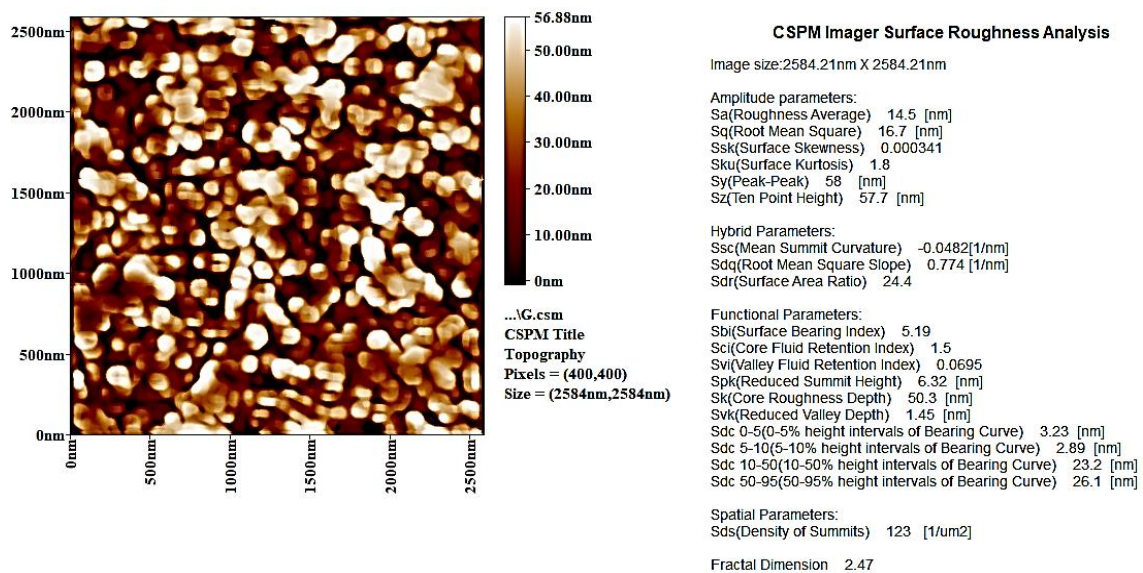

Figure 5. Image surface roughness analysis before using green algae extract.

Figure 6. Image surface roughness analysis after using green algae extract.

3.5% NaCl and without the use of green alga, the surface morphology was very rough and contained deep pits (Figure 5), while the surface when green alga was used is much smoother (Figure 6) that makes the surface less corrosive. Infrared spectrum tests were performed for green algae extract; the results were identical for both without NaCl and with the salt as shown in Figure 7. The spectrum showed the presence of two main absorption bands between 3421 cm^{-1} to 3334 cm^{-1} belonging to the hydroxyl group of protein, carbohydrate and polyphenols, as well as absorption bands in the fingerprint region 1654.81 cm^{-1} are due to the stretching frequency of the C=O bond amide I, as well as the 1080 cm^{-1} due to C-O carbohydrate while absorption bands in region 1533 cm^{-1} are due to the frequency of the C-N amide II band.
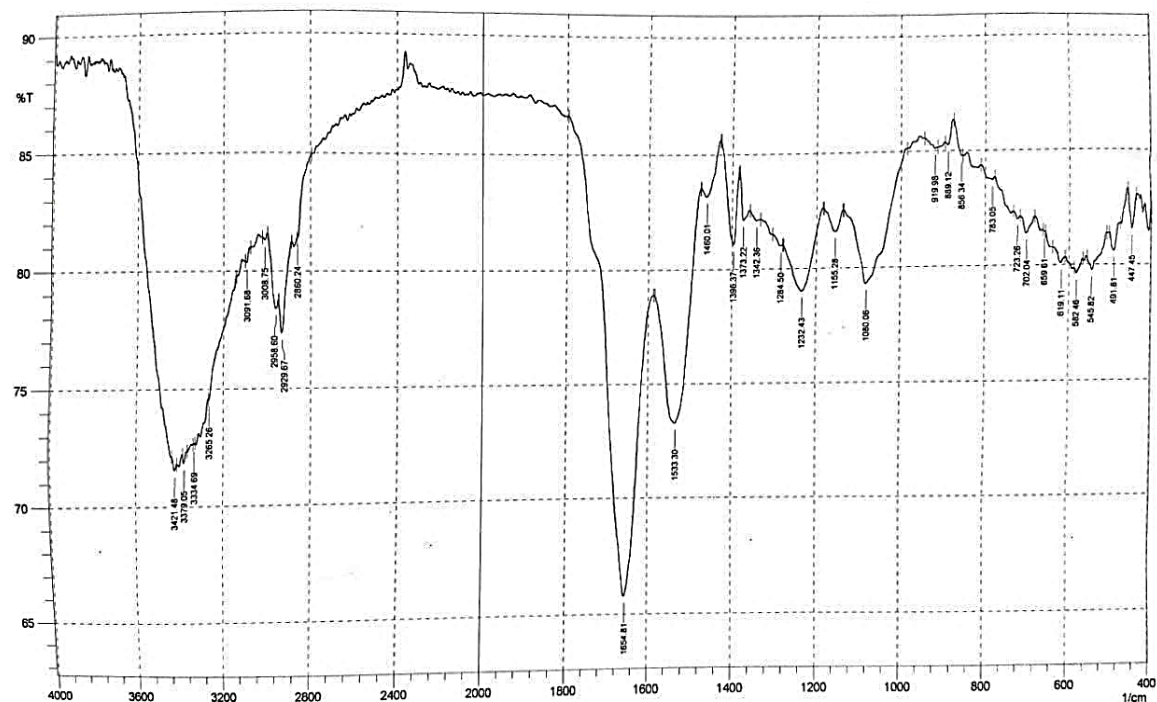
Figure 7. Infrared spectrum of green algae powder.

CONCLUSIONS

The results of this study revealed that the value of the corrosion current density increases with temperature and decreases with the concentration of dry weight of green algae. When reaching the highest level of temperature and green algae concentration, the maximum inhibitory efficiency was 99%. The estimated and experimental inhibitory efficiencies were in good agreement.

REFERENCES

1. Cherrak K, Dafali A, Elyoussfi A, El Ouadi Y, Sebbar NK, El Azzouzi M, Elmsellem H, Essassi EM, Zarrouk A. Two new benzothiazine derivatives as corrosion inhibitors for mild steel in hydrochloric acid medium. J Mater Environ Sci. 2017; 3 (2): 636–647.
2. Ouici H, Tourabi M, Benali O, Selles C, Jama C, Zarrouk A, Bentiss F. Adsorption and corrosion inhibition properties of 5-amino 1,3,4-thiadiazole-2-thiol on the mild steel in hydrochloric acid medium: thermodynamic, surface and electrochemical studies. J Electroanal Chem. 2017; 803: 125–134.
3. Ansari KR, Quraishi MA, Singh A. Schiffs base of pyridyl substituted triazoles as new and effective corrosion inhibitors for mild steel in hydrochloric acid solution. Corros Sci. 2014; 79: 5–15.
4. Sheldon RA. Metrics of green chemistry and sustainability: past, present, and future. ACS Sustain Chem Eng. 2018; 6: 32–48.
5. Rehan TA, Lami NA, Khudhair NA. Synthesis, characterization and anti-corrosion activity of new triazole, thiadiazole and thiazole derivatives containing imidazo [1, 2-a] pyrimidine moiety. Chem Method. 2021; 5 (4): 285–295.
6. Al-Azzawi AM, Yaseen HK. Synthesis, characterization and polymerization of new maleimides. Pharm Res. 2016; 8 (8): 241–247.
7. Al-Sammarraie AM. Role of carbon dioxide on the corrosion of carbon steel reinforcing bar in simulating concrete electrolyte. Baghdad Sci J. 2020; 17 (1): 0093.
8. Edyvean RGJ, Terry LA. Studies in environmental science. In: Evans LV, Hoagland KD, editors. Algal Biofouling. New York: Elsevier Science; 1986. pp. 211–230.
9. Kamal C, Sethuraman MG. *Hydroclathrus clathratus* marine alga as a green inhibitor of acid corrosion of mild steel. Res Chemical Intermed. 2012; 39 (8): 3813–3828.
10. Heitz E, Schwenk W. Theoretical basis for the determination of corrosion rates from polarisation resistance: report prepared for the European Federation of Corrosion Working Party on Physicochemical Testing Methods of Corrosion—Fundamentals and Application. Br Corros J. 1976; 11 (2): 74–77.
11. Hoar T. Electrochemical principles of the corrosion and protection of metals. J Appl Chem. 1961; 11 (4): 121–130.
12. Khudhair NA, Al-Sammarraie AM. Study the effect of SiO_2 nanoparticles as additive on corrosion protection of steel rebar in artificial concrete solution. J Eng Appl Sci. 2019; 14 (9): 10616–10621.
13. Anderson GK. Enthalpy of dissociation and hydration number of carbon dioxide hydrate from the Clapeyron equation. J Chem Thermodyn. 2003; 35 (7): 1171–1183.
14. Koutsoyiannis D. Clausius–Clapeyron equation and saturation vapour pressure: simple theory reconciled with practice. Eur J Phys. 2012; 33 (2): 295.
15. Allwright H, Enshaei H. Investigation of the impact of marine algae on the corrosion of mild steel. J Basic Appl Sci Res. 2016; 6 (3): 28–37.
16. de Souza FS, Spinelli A. Caffeic acid as a green corrosion inhibitor for mild steel. Corros Sci. 2009; 51 (3): 642–649.
17. Perez N. Electrochemistry and Corrosion Science. New York: Springer; 2004.
18. Khudhair NA, Bader AT, Ali MI, Husseini M. Synthesis, identification and experimental studies for carbon steel corrosion in hydrochloric acid solution for polyimide derivatives. AIP Conf Proc. 2020; 2290 (1): 030014.
19. Thomas S, Birbilis N, Venkatraman M, Cole I. Corrosion of zinc as a function of pH. Corros J Sci Eng. 2012; 68 (1): 015009-1–015009-9.

20. Kumbhalkar MA, Bhope DV, Vanalkar AV. Finite element analysis of rail vehicle suspension spring for its fatigue life improvement. In: Anthony K, Davim J, editors. Advanced Manufacturing and Materials Science. Lecture Notes on Multidisciplinary Industrial Engineering. Cham, Switzerland: Springer; 2018. pp. 39–53.