

Mechanism and Inhibition Efficiency of Biomass *Tetraselmis chunii* sp. on Carbon Steel Corrosion in The Environment under The Conditions of Oil Wells

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Abstract: Corrosion control on petroleum pipe wells can only be done through the addition of corrosion inhibitors. In this study, the corrosion inhibitors studied were sourced from marine microorganisms, namely the type of microalgae *Tetraselmis chunii* sp. The aim to be achieved in this study was to determine the mechanism and efficiency of inhibition of the extraction of microalgae biomass in corrosion of carbon steel in an environment of petroleum conditions. To achieve this goal, a potentiodynamic polarization method (Tafel extrapolation) was used and the Electrochemistry Impedance Spectroscopy (EIS) method used the galvanostat -potentiostat device (Voltalab 40, PGZ 301). The results obtained from this study indicate that API 5L X65 carbon steel in the petroleum environment is very significantly corroded, caused by acidic media derived from acetic acid and dissolved CO₂. The inhibition ability of the *Tetraselmis chunii* sp. Biomass extract. in line with the increasing extraction concentration reaching optimum at a concentration of 250 ppm with inhibition efficiency reaching 70%. The mechanism of inhibition takes place through the formation of a protective layer adsorbed on the surface of carbon steel. The protective membrane formed is uneven and tends to be porous.

Keyword: corrosion inhibitor, EIS/Tafel, microalgae, petroleum oil, *Tetraselmis chunii* sp.

INTRODUCTION

In petroleum mining, CO₂ saturated water is pumped into wells production to reduce viscosity and facilitate oil to get out easily (Seal S., et. Al. 2000). The crude oil produced contains inorganic salts (chlorides, sulfates and carbonates), organic acids (CH₂O₂, C₂H₄O₂, and C₃H₆O₂), and acidic gases (CO₂ and H₂S), so that when mixed with water at high temperatures being a very corrosive medium for carbon steel pipes used (Obeyesekere, et.al, 2000).

The presence of CO₂ in the media results in acidic media and triggers the occurrence of hydrogen evolution (Seal, et. Al., 2000). Although dissolved CO₂ can react with Fe to form FeCO₃ adsorbed on the surface of carbon steel and is passive, but corrosion cannot be avoided because in the media there are organic acids and chloride ions, where the species are very aggressive to be able to break FeCO₃ passive membranes (K. Videm, 2000; B. Hedges and L. Mc. Veigh, 1999).

Corrosion on the external part of the pipe could be overcome by coating or cathodic protection, but corrosion on the internal part can only be overcome by adding adsorbed type inhibitors (adsorbates), namely a chemical that is added to the corrosive environment in very little amount to control corrosion through the mechanism of forming a protective thin membrane on the surface of the internal part of the pipe (Sunarya et al., 2016).

The development of corrosion inhibitors is directed at heteroatom organic compounds containing nitrogen, sulfur, oxygen, or phosphorus. The inhibitory power of

these atoms is: P > S > N > O (Raicheva, et. al., 1992). The inhibitory ability of organic compounds is based on affinity for metals. There are three groups of organic compounds that have the potential as metal corrosion inhibitors, namely: (1) amine compounds, (2) heterocyclic nitrogen compounds, and (3) compounds containing mercapto, phosphorus, amide or thiocarbamide groups (Şahin and Bilgiç, 2003; Hesham T.M, et.al., 2016; Aprael S. Yaro, et.al., 2013).

The development of corrosion inhibitors from carbon compounds requires an understanding of the relationship between structure and adsorption properties and their mechanisms because the adsorption properties depend on the structure and electronics of inhibitor molecules, such as functional groups, steric factors, electron densities, and donor orbital characters (Ramachandran et.al., 1999; Popova, et. al., 2004; Hamdy and Nour, 2013). Corrosion inhibitors suitable for protecting petroleum wells at low acidity and high temperatures are types of adsorbates, soluble in water and oil but do not stabilize emulsions, are safe for the environment and are easily obtained at competitive prices (Tomoe, Y. and Shimizu, M., 2000).

Based on the results of the study, it is known that many functional groups of nitrogen-containing carbon compounds have high corrosion inhibition activity, especially amine compounds. Amine compounds are found in microalgae as a constituent of cell walls (Kamal dan Sethuraman, 2012). According to Greene, et al. (2006), in microalgae there are various active sites which have the potential to bind to metals, including functional groups amine, amide, imidazole, hydroxyl, phosphate, thiol, and thioether.

Microalgae are the most primitive plant-sized cellular organisms commonly known as phytoplankton. This organism is a primary producer of water that is capable of photosynthesis like high-level plants. Microalgae play an important role in food webs in marine waters and are organic matter in marine sediments (Kawaroe et al., 2010). Therefore in this study, it will be directed at certain microalgae biomass as an alternative material for metal corrosion inhibitors in the environment according to the conditions of petroleum production wells.

RESEARCH METHODS

Materials and Tools

This research uses acetone, natrium chloride (NaCl), acetate acid (CH₃COOH), sodium acetate (CH₃COOHNa), *Tetraselmis chuii* sp., distillate water, and methanol. Then, the tools functioned are carbon steels and electrode (platinum).

Procedures

Preparation of working electrodes

Carbon steel samples are taken from the type of American Petroleum Institute (API) 5L grade X65 with the following composition (in percent):

Tabel 1 Composition of samples

C	Si	S	P	Mn	Ni	Cr	Cu	W	A	Fe
0,074	0,288	0,007	0,015	1,535	0,013	0,022	0,005	0,003	0,028	97,933

Working electrodes were made by cutting the API-5L-X65 sample, turning into a diameter of 1.4 cm and a length of 2 cm, connected with copper wire, and coated with epoxy resin to obtain a surface area of 1.5 cm². Before being used as a working electrode, the electrode surface was smoothed with sandpaper (grade 400 to 1200), washed with distillate water and acetone, then dried.

Preparation of the test solution

The test solution is made by dissolving a certain amount of Merck quality chemicals p.a. into the distillate water, as follows:

The test solution (pH 3.0 0.05) was prepared by dissolving 11.7 g NaCl plus concentrated CH₃COOH and 0.146 g CH₃COONa into distillate water up to 1 liter volume (the composition of the media according to the conditions of the oil production well earth).

Preparation of the parent solution of *Tetraselmis chuii* sp. (1×10⁴ ppm). In 100 mL of distillate water methanol extracted from *Tetraselmis chuii* sp. as much as 1.0 ± 0.003 g.

Testing Procedure

Poured into 250 ml electrochemical cell NaCl solution, continuously bubbled with CO₂ at a pressure of 0.25 ± 0.05 atm and stirred with a magnetic stirrer at a speed of 400 rpm. The working electrode (carbon steel), the reference electrode (saturated calomel electrode, SCE), and the auxiliary electrode (platinum) dipped in the test solution and connected to the potentiostat from Radiometer® (Voltalab PGZ 301). Before being measured, the cell is left for 1 hour so that the carbon steel / media interface reaches a steady state. *Tetraselmis chuii* sp. Concentration tested 0.01 mM and the temperature of the system is controlled by a thermostat. Output data from the measurement results are processed using the Voltmaster program 4 version.

In the measurement with the EIS, the sine wave signal is applied to disrupt the system are generated from AC potential with the amplitude of 10 mV (ASTM G3, 1989) and a frequency range from 100 kHz applied to 10 mHz. In polarization measurements, the applied DC potential is ± 50 mV relative to the corrosion potential value. The polarization curve is recorded with a constant sweep rate at 0.5 mV.s⁻¹ (ASTM G5, 1987).

The results of the potentiodynamic polarization curve were extrapolated by the Tafel technique to obtain the corrosion potential, Tail (mV), polarization resistance, Rp (Ω.cm²), anodic constant, β_a and cathodic, β_c (mV.dec⁻¹). Based on these values the corrosion current density, *I*_{corr} (Ω A.cm⁻²) is determined by equation 1 and the corrosion rate, V_{corr} (mm.y⁻¹) from the equation 2

$$I_{kor} = \frac{\beta_a \cdot \beta_c}{2,303(\beta_a + \beta_c)} \frac{1}{R_p} \quad (1)$$

$$V_{kor} = 0,00327 \frac{A_r}{n \rho} I_{kor} \quad (2)$$

A_r is the relative atomic mass of metal, n is the number of electrons involved in corrosion, and ρ is the density of the metal. Determination of inhibition efficiency (% EI) is based on corrosion current density, I_{corr} according to equation 3.

$$EI(\%) = \left(1 - \frac{I_{kor}^{Inh}}{I_{kor}^0} \right) \times 100 \quad (3)$$

The impedance spectra from EIS measurements are expressed in the form of Nyquist, which expresses the relationship between imaginary impedance, $Zi_{(w)}$ as a function of real impedance, $Zr_{(w)}$. Furthermore, the spectra are processed by circular regression to obtain the resistance value of the solution (R_s), charge transfer resistance (R_{ct}), and multiple layer capacitance (C_{dl}).

RESULT AND DISCUSSION

Measurement of Potentiodynamic Polarization

Based on the measurement of potentiodynamic polarization, the relationship between corrosion potential and corrosion current is obtained, which is then processed by the Tafel extrapolation technique to produce a graph as shown in Figure 1. Based on the graph it can be seen corrosion potential, E_{corr} , corrosion current density, I_{corr} , Cathodic Tafel constant, β_c and the anodic Tafel constant, β_a , and the corrosion rate carbon steel in the test solution, V_{corr} . Data from extrapolation from Tafel are presented in table 2

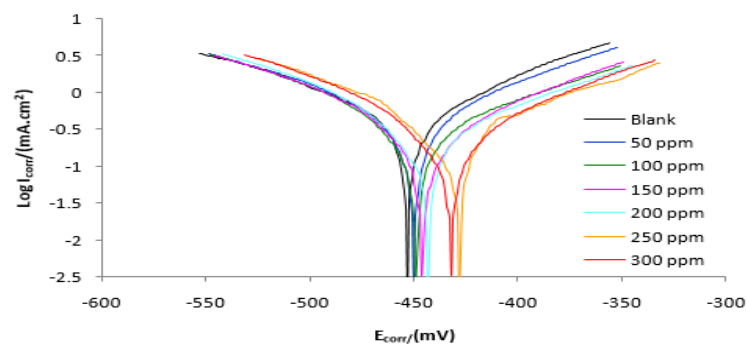
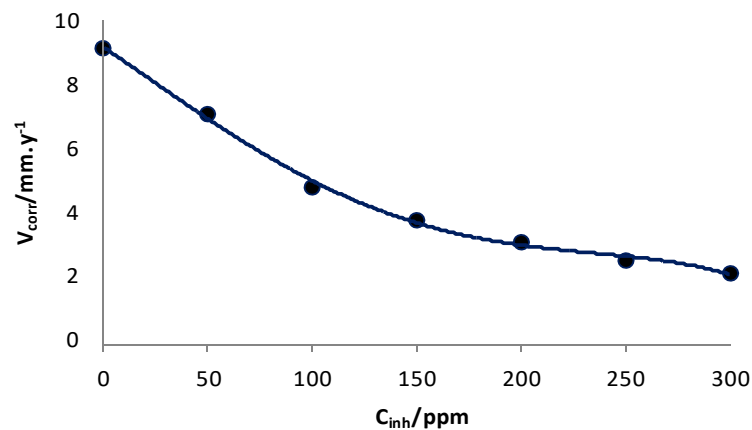


Figure 1. Corrosion potential and the logarithm of corrosion current density for carbon steel in the test media with and without *Tetraselmis chuii* sp.

Table 2. Parameters of corrosion of carbon steel in the test solution and potential inhibition of the methanol extract of *Tetraselmis chuii* sp.

$C_{inh}/(\text{ppm})$	$E_{corr}/(\text{mV})$	$\beta_a/(\text{mV/dec})$	$\beta_c/(\text{mV/dec})$	$I_{corr}/(\mu\text{A}/\text{cm}^2)$	$V_{corr}/(\text{mm}/\text{y})$
-	-454.3	110.7	135.6	0.7764	8.9992
50	-450.3	109.8	122.6	0.6013	6.9766
100	-448.6	105.9	92.1	0.3622	4.2021
150	-444.9	98.2	88.3	0.3168	3.6761
200	-443.4	95.1	84.1	0.2596	3.0122
250	-432.3	94.9	81.3	0.2119	2.4580
300	-429.9	93.2	77.2	0.1992	2.0714

The corrosion rate of carbon steel in the test solution (0.2 M NaCl solution saturated with CO₂ gas bubbling and its pH is controlled by an acetate buffer of 3.0 ± 0.05) reaching 9 mm per year. This means that the corrosion of carbon steel surface by a test solution in one year is 9 mm thick. Addition of *Tetraselmis chuii* to the test solution reduced the corrosion rate of carbon steel to 2.07 mm per year. The inhibition ability of *Tetraselmis chuii* on corrosion of carbon steel in the test solution is shown in Figure 2.

Figure 2. Decreasing the corrosion rate of carbon steel in a test solution by *Tetraselmis chuii* sp

The decrease in corrosion rate with the presence of *Tetraselmis chuii* indicates that the addition of *Tetraselmis chuii* to the test solution can reduce the energy level of the outer electrons on the surface of carbon steel which results in a decrease in the metal's outer electrons (Sato, 1987), so that the corrosion rate carbon steel decreases. In other words, the formation of Fe²⁺ ions on the surface of carbon steel is inhibited by the presence of microalgae.

Before *Tetraselmis chuii* was added to the solution, value of E_{corr} , was -454.3 mV. After addition, the corrosion potential value shifts towards a more positive direction, as in Figure 3. This shows that the presence of *Tetraselmis chuii* lowers the energy level of the

electron by shifting the corrosion potential in a more positive direction. This shift shows that the inhibition mechanism of *Tetraselmis chuii* through inhibition of anodic oxidation process by forming a protective layer on the metal surface. Decreasing electron energy levels on carbon steel surfaces give the opportunity for molecules extracted from *Tetraselmis chuii* to act as Lewis bases or van der Waals styles (Singh, et.al., 2016; Al-Otaibi, 2014).

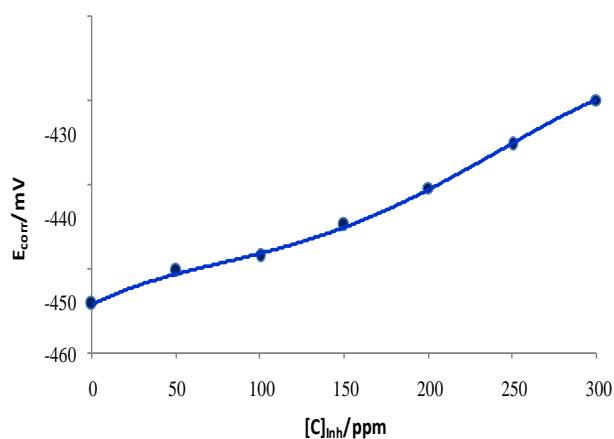


Figure 3. Effect of the addition of *Tetraselmis chuii* to the corrosion potential of carbon steel

Observing the values of anodic Tafel (β_a) and cathodic (β_c) which are constants, the *Tetraselmis chuii* can reduce both the values β_a and β_c . This indicates that the corrosion inhibition mechanism, other than through anodic processes, also through increasing the potential barrier energy to inhibit the hydrogen evolution reaction in the cathodic process, so that the electron transfer rate from the carbon steel surface to the H^+ ions is inhibited or by binding H^+ ions by extract *Tetraselmis chuii* (hydrogen scavenger), consequently the rate of formation of H_2 gas in the solution is inhibited. Thus, *Tetraselmis chuii* is classified as a mixed type inhibitor.

The presence of *Tetraselmis chuii* in the test solution decreases the corrosion density current value, I_{corr} . The more concentration of *Tetraselmis chuii* is added, the smaller the value of I_{corr} , so that the corrosion rate of carbon steel decreases. The optimal concentration achieved by *Tetraselmis chuii* in inhibiting corrosion of carbon steel is approximately 250 ppm with inhibition efficiency reaching 70%, as shown in figure 4.

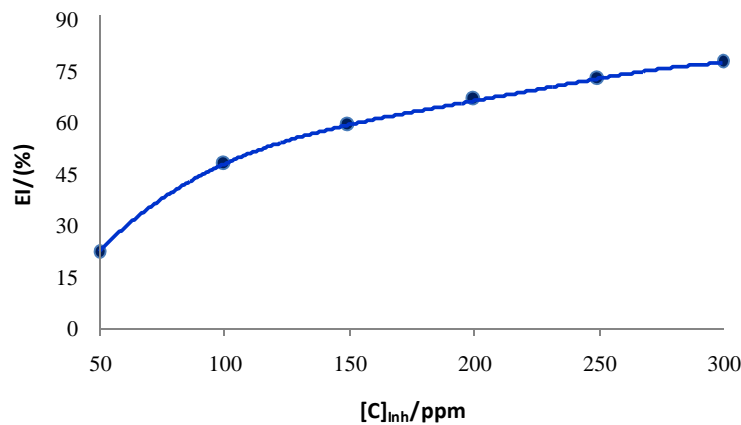


Figure 4. Relationship between inhibition efficiency and *chuii* *Tetraselmis* concentration based on the results of polarization measurements

Impedance Measurement

Measurement data using the EIS method in the form of impedance spectra are expressed in the form of a Nyquist diagram, this diagram states the relationship between real impedance, Z_r and imaginary impedance, $-Z_i$ (Figure 5). Furthermore, the data is processed using a circular regression technique to obtain electrochemical parameters in the form of solution resistance, R_s , charge transfer resistance, R_{ct} , and double-layer capacitance, C_{dl} , presented in Table 2. The form of an impedance diagram in the form of semi-circular, which indicates that the carbon steel corrosion process is controlled by the transfer of cargo. However, the impedance diagram is not really semi-circular, this is caused by the presence of dispersion at high frequencies.

The presence of *Tetraselmis chuii* in the relative test solution does not change the resistance of the solution. That is, *Tetraselmis chuii* is not an ionic compound but in the form of a polar molecule so that the solution resistance or electrical conductivity is relatively constant. On the other hand, the addition of *Tetraselmis chuii* can increase the charge transfer

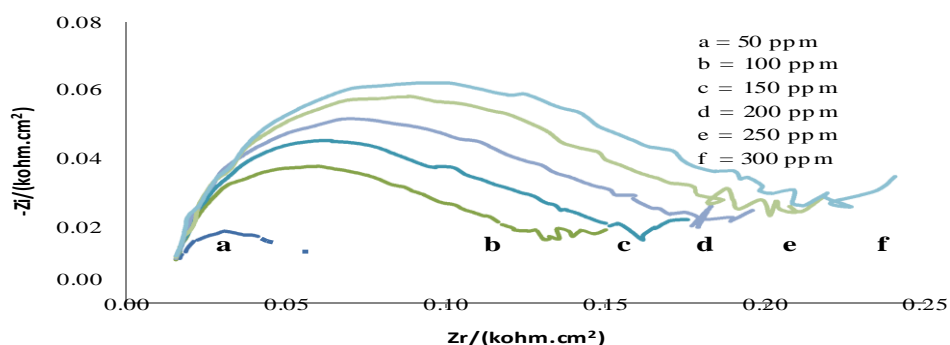


Figure 5. Carbon steel impedance spectra in the test solution with and without *Tetraselmis chuii* sp. at various concentrations

Resistance on carbon steel surfaces, which results in the reduction of hydrogen ions and the oxidation process of Fe atoms at the metal interface and the solution becomes inhibited, so the corrosion rate of carbon steel decreases

Table 3. The electro-kinetic parameters of carbon steel in the test solution with and without *Tetraselmis chuii* sp.

$C_{Inh}/(mM)$	$R_s/(\Omega \cdot cm^2)$	$R_{ct}/(\Omega \cdot cm^2)$	$C_{dl}/(\mu F/cm^2)$
-	13,54		194,6
50	12,38	110,30	175,0
100	12,00	144,60	162,5
150	11,60	177,60	151,5
200	11,48	210,60	149,4
250	11,23	238,20	135,8
300	11,11	278,60	124,2

Double-layer capacitance is obtained at the maximum frequency, f_{maks} , ie when the value of the imaginary component of the impedance reaches its maximum, $-Z_{i(maks)}$, according to the following equation (Loveday, 2004):

$$f(-Z_{i(maks)}) = \frac{1}{2\pi C_{dl} R_{ct}} \quad (4)$$

The carbon steel response to impedance has changed dramatically in the presence of *Tetraselmis chuii* and its frequency has increased with increasing its concentration. As a result, the value of double layer capacitance is significantly reduced. The decrease in value can be caused by the presence of *Tetraselmis chuii* adsorption on the surface of carbon steel to form a protective layer which is insoluble so that there is a decrease in the local dielectric constant.

Equivalent electrical circuit model at the interface

To interpret the electrical properties at the interface between carbon steel and the test solution can be studied through the Zview program from Scribner Associates. This is done by means of curve fitting the impedance spectra measurement results with impedance spectra curve simulation models developed equivalence electrical circuits (Loveday 2004). Based on the simulation results of electric circuit models it is known that the interface of carbon steel with the test solution without the presence of *Tetraselmis chuii* has an electric circuit model as shown in figure 6 (a).

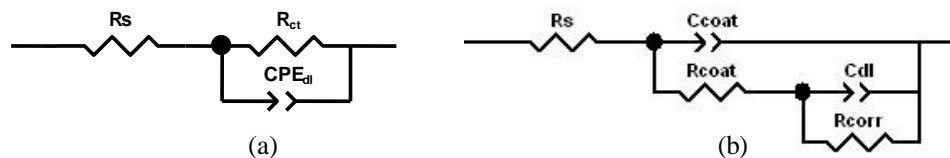


Figure 6: Electrical circuit model equivalent to the carbon steel interface and test solution.
(a) Without microalgae; (b) contains microalgae.

The electrical circuit model in Figure 6.a consists of solution resistance, charge transfer resistance, and multiple layer capacitances, CPE_{dl} , at the metal interface and solution. Such circuit models show that the corrosion rate of carbon steel is controlled by the rate of charge transfer reaction. Symptoms like this are commonly found when a metal is dipped in a solution, where a protective layer has not been formed. The presence of *Tetraselmis chuii* changes the circuit model as shown in figure 6 (b), and applies to all *Tetraselmis chuii* concentrations added to the solution. The model indicates that on a carbon steel surface a protective layer is formed from the extract of methanol *Tetraselmis chuii* which is imperfectly adsorbed with layer resistance and double layer capacitance indicated by R_{coat} and C_{coat} . Imperfection is indicated by the presence of multiple electrical layer capacitances between the protective layer and the carbon steel surface.

Based on the equivalent electrical circuit model it can be stated that *Tetraselmis chuii* can inhibit the corrosion of carbon steel in the test solution by forming a protective layer on the surface of carbon steel. However, the protective layer formed is not perfect because there are still a number of pores that can be penetrated by the species in the solution so that the inhibitory efficiency is less effective.

CONCLUSIONS

The corrosion rate of API-5L-X65 carbon steel in a solution that is in accordance with the conditions of petroleum production wells reaches a thickness of 9 mm per year. Addition of *Tetraselmis chuii* sp. into the test solution can reduce the corrosion rate to 2.07 mm per year with a percent efficiency of inhibition of 70% for the concentration of *Tetraselmis chuii* 250 ppm. *Tetraselmis chuii* is a mixed type inhibitor. The mechanism of inhibition is through the formation of protective layers that tend to be still porous.

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