Black Tea Waste as Corrosion Inhibitor for Carbon Steel in 0.5 M HCl Medium

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Abstract: Indonesian black tea (BT) waste was utilized as a green corrosion inhibitor for carbon steel (CS) corrosion in a 0.5 M HCl medium. The BT extract was characterized using Fourier transform infra-red. The corrosion inhibition evaluation was studied using conventional weight loss methods, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). Further, scanning electron microscopy-energy dispersive X-ray was applied to analyze the surface morphology of pure CS before and after contact with the inhibitor extract. After the addition of inhibitors, CS surface showed a better morphological transformation. The effect of oxygen contamination has also been studied in this research. The corrosion measurements of weight loss, potentiodynamic polarization, and EIS showed that the %IE BT extract was 84.70; 70.00; 72.80% at 0.20 g/L of inhibitor concentration. Adsorption isotherm studies have determined the reaction mechanism between the CS and inhibitor; in which the adsorption follows Langmuir. Gibbs free energy for the three methods is −16.62; −25.34; −24.35 kJ/mol, indicating electrostatic interaction (physisorption) between the metal surface and inhibitor. SEM and focus ion beam show that oxygen contamination can increase the corrosion rate resulting in CS damage. It shows that tea waste products can be used as an alternative corrosion inhibitor.

Keywords: black tea; carbon-steel; corrosion inhibitor; potentiodynamic polarization; electrochemical impedance spectroscopy

■ INTRODUCTION

The application of carbon steel (CS) has been increasing in the industry because CS has good mechanical properties. Some examples of CS applications include automobile components, structural shapes, and sheets used in pipelines, buildings, plants, and bridges [1-2]. In contrast, metal corrosion is a significant dilemma for engineering materials utilization in various environments [3]. In particular, the oil and gas industries involve chloride ions from water formation during drilling. The presence of chloride ions and impurities CO_3^{2-}, which is engaged in drilling, causes these anions to react with H^+ to produce HCl and H_2CO_3, which are corrosive compounds. So, HCl is used for corrosive environmental conditions to represent the actual conditions in the field [4].

Severe corrosion damage has been developing into a significant global problem due to plant closures, a massive waste of revenue, product disruption, reduced efficiency, and expensive repairs. Corrosion also endangers safety and hinders technological

development, where corrosion can crush substances by reacting with their environment [5]. The reparations of corrosion are costly. It can also cause hazardous damage to infrastructure, waterways, ports, railroads, unsafe materials storage, fresh water, sewage systems, electrical services, cars, ships, aeroplanes, petroleum refineries, gas transmission pipelines, and bridges. Thus, ongoing efforts are to evolve protective tools that protect the materials effectively from corrosion. Various corrosion prevention methods have been developed, including material selection, protective coatings, cathodic protection, and corrosion inhibitors [6]. Corrosion inhibitors were chosen in this study because of cheaper and easier to prepare and have good efficiency [7-8]. The materials are called corrosion inhibitors to minimize corrosion [9].

Inhibitors are chemicals that stop or reduce corrosion when mixed with minerals in minimal amounts and do not react with environmental components. Inhibitor molecules will form an active film layer on the region along the pipe wall to reduce the direct interaction between the fluid and pipe so that corrosion reactions can be minimized. Organic compounds that have electronegative functional groups and π-electron in triple or conjugated double bonds are excellent inhibitors. When the aromatic ring contains nitrogen, sulfuric, phosphorus, and oxygen; they become the primary adsorption centers.

On the other hand, such compounds are not environment-friendly and are carcinogenic because they contain functional aromatic groups. However, this type of organic inhibitor has several weaknesses; in a few concentrations, the inhibitor can initiate the corrosion reaction or, at a high inhibitor concentration, will cause coagulation, so besides being able to accelerate the corrosion reaction, this type of inhibitor will affect the quality of oil and gas products. To overcome this problem, searching for types of natural inhibitors with high inhibition efficiency and are environmentally friendly is continuously being carried out. Natural inhibitors are environmentally friendly because they are derived from plant extracts.

Plant extracts perform good ability to inhibit surface metal corrosion by a simple, safe, and inexpensive

procedure following the principle of green chemistry. Aconitine and tubocurarine alkaloids [10], green tea [11], coconut husk [12], tree bark [13], and Lipton black tea as corrosion inhibitors have been reported [14]. The compounds come from plant extracts that have high tannin composition. Therefore, they are used as the inhibitor of corrosion, as mentioned in previous research.

Tannins in mangrove plants and chestnuts are able to inhibit metal corrosion [15]. Tannins from plant extracts are non-toxic, biodegradable and can bind proteins, alkaloids, and polysaccharides. The hydroxyl groups of tannin act as excellent inhibitors. It can produce chelates with metallic cations. The inhibiting properties came from a highly cross-linked network between the metallic surface and OH groups [16]. Because the tannin composition is present in black tea (BT), BT was used as an inhibitor of CS corrosion in this study.

Tea is one of the famous beverages in Indonesia. Based on the level of fermentation, tea can be classified as green tea and BT [17]. BT is produced about 78% comprehensively due to the high demand in some world continents, especially in Indonesia [18]. BT contains tannins, flavonoids, phenolic acids, caffeine, amino acids, and others. Because of that composition, it has many health benefits, has antioxidant activity, lowers cholesterol level, resolves digestive problems, improves poor blood circulation, and so on [19]. Un-useful BT waste will be raised its economic value.

Tannin from Indonesian BT waste was extracted and studied for CS corrosion inhibitors. Hence, the corrosion inhibition potential of BT extract for CS protection was screened and reported here. The standard corrosion monitoring techniques viz., weight loss and electrochemical (EIS and potentiodynamic polarization) methods were employed for this purpose. Further, surface morphology screening was carried out on the CS surface before and after the corrosion process via SEM-EDX and focus ion beam (FIB) analysis.

■ EXPERIMENTAL SECTION

Materials

The devices used in this work were easy to be accessed in many laboratories. The materials include

acetone (99% purity Merck, Germany), aquadest, and black tea were brought from a local market in Indonesia.

Instrumentation

The electrochemical study was carried out using Gamry Reference 600 Instruments software (potentiostat/galvanostat/ZRA). The FTIR analysis uses a Perkin Elmer System 2000 instrument in 400 to 4000 cm^{-1}. SEM SU3500 instrument was used for the morphology and elemental analysis. FIB (BIM FIB TESCAN LYA3 using an energy beam of 5 keV) was also used.

Procedure

Inhibitor preparation

BT powder (1 g) is stirred with 100 mL of hot water. The tea is filtered so that the residue in tea waste is obtained. The tea waste received is then dried at room temperature and mashed with a mortar. One gram of BT waste powder was placed in a vessel, and then 50 mL of acetone was used as a solvent. The vessel is placed in the microwave with a power of 250 W for 6 min. The extract was filtered to separate the filtrate from the residue. The extract was evaporated to the next corrosion inhibition activity.

Specimen preparation

The composition of CS specimens 1018 are 97.57; 1.54; 0.88 wt.% for Fe, C, and O, respectively, were prepared and polished using abrasive papers with different grades from 400 up to 1200 before the analysis. Weight loss studies used the size of the CS specimens $2.7 \times 2.7 \times 0.1$ cm. The specimen exposed area (1 cm^2) was used for EIS and potentiodynamic polarization studies.

FTIR analysis

FTIR analyzed the BT extract to identify functional groups of inhibitors. The pellet was prepared by compressing the sample with KBr (the ratio of the sample to KBr 1:10).

Weight-loss method

The cleaned and sanded CS specimens were then dried in acetone. CS was then weighed and immersed in 0.5 M HCl (Beaker A). While for Beaker B, CS was dipped in 0.5 M HCl solution and inhibitor. The duration time is 7 d at room temperature (30 °C). CS specimens were then

cleaned with aquadest, acetone and dried, respectively. The experiment was done in triplicate. The calculation of inhibition efficiency (IE) can be seen in Eq. (1), as explained in ASTM G31;

$$IE_{WL}(\%) = \left(1 - \frac{W_i}{W_0}\right) \times 100 \tag{1}$$

where W_0: weight lost from the steel sample without inhibitor (g) and W_i: lost weight of steel sample with inhibitor (g).

Electrochemical studies

A cell system containing three electrodes is used. The working electrode (WE) is an area of 1 cm^2 of CS. The used counter electrode and reference electrode were saturated calomel electrodes (SCE) and platinum wire, respectively. The experiment was carried out in 0.5 M HCl solution with or without adding some inhibitor concentrations in and without an aerated environment. The polarization and impedance curves were documented at room temperature (30 ± 2 °C). The electrodes were used in the cell-containing solution for 30 min at the natural potential to obtain stable conditions. EIS was performed at corrosion potential (E_{corr}) with a frequency range from 0.1 to 10,000 Hz at an amplitude of 10 mV. Nyquist diagram shows the impedance. The inhibitory efficiency is analyzed using charge transfer resistance (R_{ct}) (Eq. (2)).

$$IE(\%)_{eis} = \left(1 - \frac{R_{ct(0)}}{R_{ct(i)}}\right) \times 100 \tag{2}$$

Potentiodynamic current density vs. potential was recorded using a scanning electrode potential (between −800 to −200 mV (vs. SCE)) with 10 mV/s scanning rate. The corrosion current density (I_{corr}) was achieved by plotting the linear Tafel segments extrapolation of the anodic and cathodic and the corrosion potential. The calculation of pct IE from I_{corr} was shown in Eq. (3) [20].

$$\%I_{pp} = \left(1 - \frac{I_{corr(i)}}{I_{corr(0)}}\right) \times 100 \tag{3}$$

Adsorption isotherm studies

The adsorption of BT extract onto the CS surface in 0.5 M HCl medium was studied in adsorption isotherm plots. Adsorption isotherms were studied for weight loss, potentiodynamic polarization, and EIS. The X-axis

is the inhibitor concentration (0.05; 0.10; 0.15; 0.20 g/L), and the y-axis is C/θ. θ is obtained from the ratio IE/100. The adsorption isotherm curves were plotted onto the isotherm models of Langmuir, Temkin, and Frumkin.

Study of SEM-EDX

The surface morphology of the WE was then characterized by using SEM, which was carried out at an optimum concentration (0.20 g/L) of BT extract. After the electrochemical measurements, the specimen was removed from the system, gently rinsed with aquadest then dried.

FIB analysis

To observe the process of corrosion below the surface of the corroded material, FIB was used. Ion gallium was used as a beam and produced a secondary electron after being attached to the specimen surface. The samples were masked with a conductive thin layer of Pt (~10–20 nm).

■ RESULTS AND DISCUSSION

FTIR Study

Functional groups in BT extract were studied by FTIR spectroscopy. Fig. 1 and Table 1 describe the infra-red absorption spectra of BT extract, O–H, C=C (for the aromatic ring), and C–O, shown at 3400 to 3100, 1640, and 1161 to 1010 cm^{-1}, respectively. Several researchers have reported these functional groups can inhibit corrosion effectively in organic corrosion inhibitors [21-22]. It has been assumed that the BT extract has many hetero-functional groups and a phi electron cloud which functions as a corrosion inhibitor. Therefore, the functional group is assumed to act as the inhibitor because it has an aromatic ring containing an OH group. Few previous research also reported a similar spectrum [21-23].

The corrosion rate inhibition mechanism can occur due to the formation of O–H and N–H (polar bonds). It can bind through an adsorption process to the CS surface. Meanwhile, the non-polar (alkyl) part of the inhibitor aggregate binds to other free hydrophobic groups in the solution. Inhibitors generally work to control corrosion reactions by creating a thin film on the CS surface. Another possible protection mechanism is the adsorption process of the inhibitor into the CS surface to form a film.
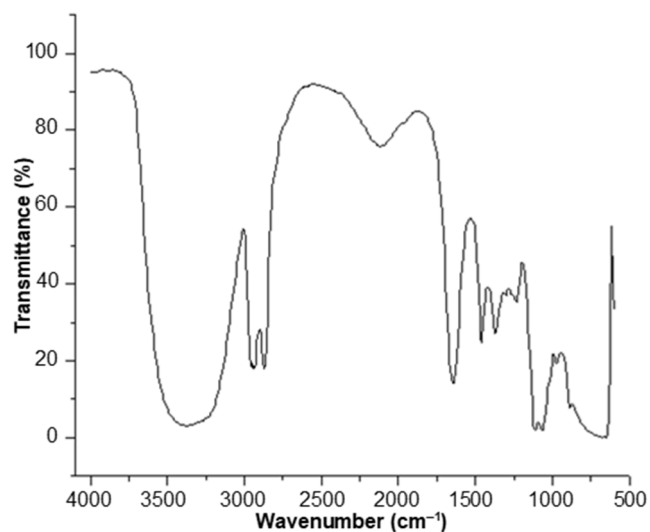

Fig 1. IR spectral of BT extract

Table 1. FTIR spectral data of BT extract

Functional group	Wavenumber (cm^{-1})
C=C (stretch)	1640 (s), 1404 (s)
C–H (stretch)	2858 (w)
O–H (stretch)	3281 (s, br)
C–O (C–O–C stretch)	1285 (m)

This thin layer can protect the steel by limiting the access to charge exchange between the electrolyte solution and the CS surface. The diffusion process becomes minimal because the transfer of ions between the solution and the metal is limited. The metal is then said to be passivated.

Weight Loss Measurement

The weight loss study of the CS specimen was measured to calculate the corrosion rate as a percent inhibitory efficiency (%IE). The IE collected for some concentrations of BT extract are shown in Table 2. The results show a positive correlation between BT extract concentrations and inhibition efficiency for CS in a 0.5 M HCl solution. This trend came from the number of adsorbed inhibitor molecules on the CS surface, increasing BT extract concentration so the CS surface is actively protected from HCl. The results of this study follow previous studies [24]. When the inhibitor concentration rises, the inhibition efficiency develops. The maximum IE value was obtained at the maximum BT extract concentration of 0.20 g/L, and the inhibition efficiency showed (84.73%). When the concentration

reached more than 0.20 g/L, %IE decreased significantly. It is probably due to the coagulation of the corrosion inhibitor molecules, which affects the interfacial reaction between the BT and the CS surface.

Potentiodynamic Polarization

Polarization potentiodynamic measurements have been done. The corrosion inhibition mechanism is achieved with this study. The electrochemical polarization observations are depicted as a Tafel curve plot, as shown in Fig. 2. Several corrosion parameters, including the potential corrosion (E_{corr}), and corrosion current density (I_{corr}), are determined using the anodic and cathodic Tafel lines intersection (Table 3).

The polarization studies show that BT extract decreases corrosion current density (I_{corr}), characterized by reduced corrosion rates. A reduction in aggressive acid attacks on the surface of the CS probably causes a decrease in I_{corr} value. It is due to the adsorption of CS into the inhibitor molecule. From Fig. 2, it can be shown that the concentration addition of BT extract (0.05 to 0.20 g/L)

shifted the corrosion potential to a positive value (from −464 to −457 mV) because the anodic reaction went down. It indicates that 0.20 g/L of the inhibitor concentration has been adsorbed towards the anodic side of the CS surface, which prevents the dissolution reaction of the metal and can control the corrosion process. Based on the table, the IE pct value increased when the
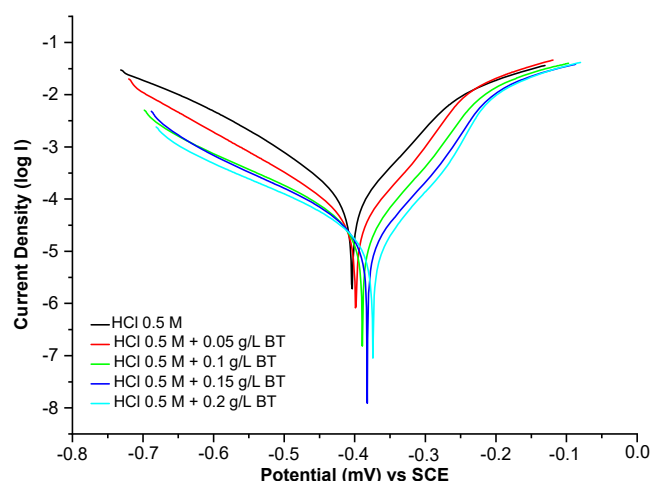

Fig 2. Tafel plot of BT inhibitor on CS in 0.5 M HCl

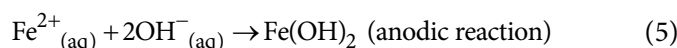**Table 2.** The inhibitory efficiency of BT waste extract for corrosion of CS in 0.5 M HCl solution

Concentration (g/L)	Weight before (g)	Weight after (g)	Weight loss (g)	%IE
0	2.9994	2.9555	0.0439	0
0.05	2.9448	2.9197	0.0251	25.80
0.10	2.9226	2.9013	0.0213	54.60
0.15	2.8986	2.8847	0.0139	68.33
0.20	2.8923	2.8112	0.0811	84.70

Table 3. Polarization study of inhibitor into CS specimen

	Inhibitor concentration (g/L)	E_{corr} (mV)	I_{corr} (µA cm^{-2})	% of IE
	Blank	−397.8	80.9	-
BT	0.05	−399.6	41.3	48.80
	0.10	−389.5	33.1	60.20
	0.15	−382.2	26.6	62.30
	0.20	−374.5	16.1	70.00
	Inhibitor concentration (g/L)	E_{corr} (mV)	I_{corr} (µA cm^{-2})	% of IE
	Blank	−429.8	98.4	-
BT with oxygen contamination	0.05	−417.6	58.8	40.24
	0.10	−404.5	50.6	48.58
	0.15	−398.2	44.1	55.18
	0.20	−393.5	33.6	65.82

BT tea extract concentration increased to 0.20 g/L. The results obtained support the effects of weight loss measurements. The inhibitory efficiency obtained is comparable to previous studies [25], which used the LPR (Linear polarization resistance) technique with flowing fluid conditions with a maximum inhibitor efficiency of 85%. The presence of oxygen contamination at BT reduces the %IE to be lower than without oxygen contamination.

Possible mechanism reaction of pipelines in the oil and gas industry that contain impurities (water, CO_2, and H_2S) in the Eq. (4-6):

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{4}$$

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_2 \text{ (anodic reaction)} \tag{5}$$

The $Fe(OH)_2$ further reacts with available oxygen and water

$$4Fe(OH)_{2(aq)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 4Fe(OH)_{3(s)} \tag{6}$$

(anodic reaction) (rust)

The presence of oxygen contamination will cause a higher corrosion rate so that the %IE is lower. At the same time, corrosion protection by inhibitors is based mainly on modifying metal surfaces by the adsorption of inhibitor molecules and the subsequent formation of a protective (blocking) monolayer. The corrosion inhibitors (tannin) contain hetero atoms such as nitrogen, sulfur, phosphorus, and oxygen atoms. Hetero atoms, i.e., oxygen – bind with the metal surface through adsorption and reducing corrosion. The hetero groups of tannin bonding with the steel surface reduces corrosion (%IE becomes high).

EIS Measurement

The corrosion resistivity of the BT sample was analyzed using EIS. The Nyquist plot of the inhibitor is shown in Fig. 3 and 4. The parameters of impedance, including charge transfer resistance (R_{ct}) and Constant Phase Element (CPE), are analyzed based on impedance plot analysis using circuits of equivalent. The complete values are in Table 4. From the results, it can be observed that the Nyquist plot shows the shape semicircle and the capacitive loop diameter increases due to the development of inhibitor concentration. It means an increase in the surface coverage of the metal and the process of charge transfer as the primary factor in corrosion.
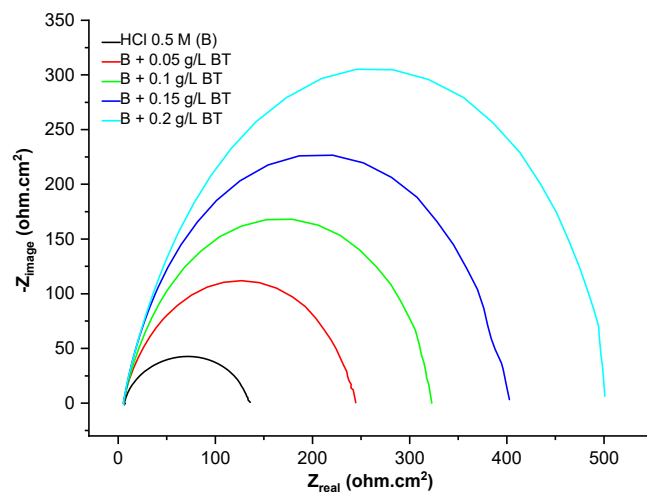

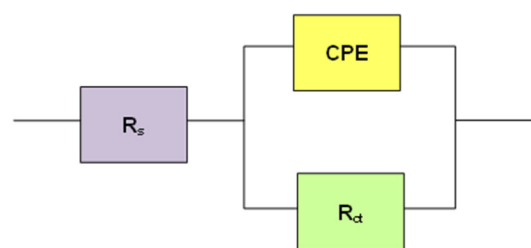**Fig 3.** Impedance measurement for BT waste inhibitors

Fig 4. Equivalent circuit model for Nyquist plots

The R_{ct} value rises with the expansion of inhibitor concentration (Table 4). The possible explanation is as follows: increasing inhibitor concentration makes the adsorption of the phytoconstituents over the surface of the CS. Therefore, the formation of a protective layer occurs and can reduce the electron transfer between the metal surface and the corrosive medium. The R_{ct} value increases with increasing inhibitor concentration. At a BT concentration of 0.05 to 0.20 g/L, the R_{ct} value increased to 499 ohms cm^2.

CPE value decreased when the concentration of inhibitor grew up. It is possibly caused by the increasing number of inhibitors and the adsorption phenomenon also growing and reducing the electrical capacity so that the electrical double layer gets thicker. From Table 4, it can also be identified that the %IE value in the EIS study rose when the inhibitor concentration gained from 0.05 to 0.20 g/L (82.8). The measurement results of this EIS method support the study of polarization potentiodynamic. In general, a weight loss study measures the corrosion rate of naturally occurring corrosion. While

Table 4. Effect of BT extract on CS (impedance study)

Inhibitor	Inhibitor concentration (g/L)	R_{ct} (ohm cm^2)	CPE (μF cm^{-2})	IE %
-	0	135.90	140.2	-
BT	0.05	241.60	79.6	43.70
	0.10	322.90	57.5	57.90
	0.15	401.10	48.9	66.10
	0.20	499.10	39.1	72.80
-	0	105.07	121.2	-
BT with oxygen contamination	0.05	165.01	84.6	36.32
	0.10	197.31	65.1	46.75
	0.15	243.91	52.2	54.62
	0.20	268.05	47.9	55.80

EIS is electrochemically induced corrosion, and further the measurement time is also different in both techniques. This may cause a deviation in the corrosion rate measurement.

Adsorption Isotherm Studies

The isotherms of adsorption were done to analyze the reaction mechanism among inhibitors and CS. C/θ vs. the concentration of inhibitor plots produce a straight curve with a correlation coefficient near 1. It can be explained that the inhibitor adsorption follows Langmuir adsorption (Fig. 5 and Table 5) for weight loss, polarization, and EIS studies. The calculation of the constant of the adsorption (K_{ads}) is in Eq. (7):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{7}$$

$$\Delta G^0_{ads} = -RT \ln C_{water} K_{ads} \tag{8}$$

where C is the concentration of the inhibitor (g/L), θ is the surface coverage (IE/100), K_{ads} is the constant of equilibrium, and ΔG^0_{ads} is the standard Gibbs free energy, R is the gas molar constant, T is temperature, and C_{water} is the water concentration in 1000 g/L. ΔG^0_{ads} is calculated from the Eq. (8).

The value of ΔG^0_{ads} from the conventional and electrochemical methods are depicted (Fig. 5). K_{ads} can be calculated from the intercept value. K_{ads} calculation results were obtained at 7.3368; 23.419; 15.773 g/L. So the calculated value of ΔG^0_{ads} is −16.62; −25.34; −24.35 kJ/mol.
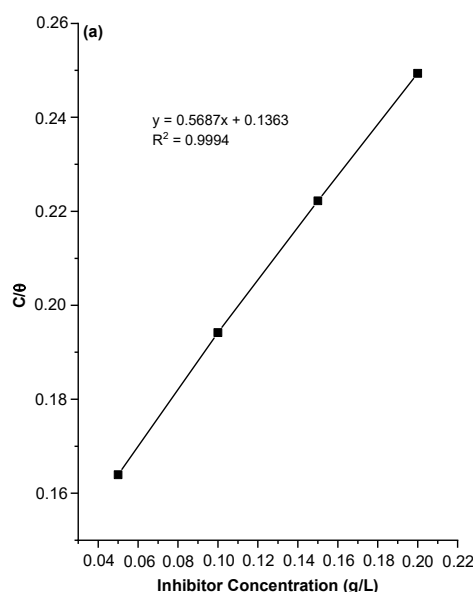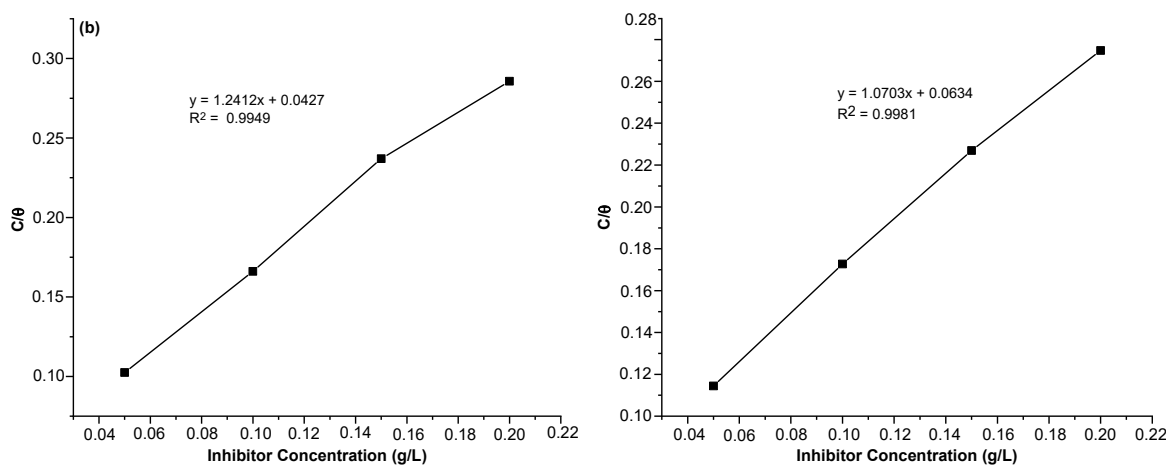
Fig 5. BT Extract of the Langmuir isotherm of adsorption on the CS surface from (a) weight loss, (b) potentiodynamic study, and (c) EIS study

Table 5. Thermodynamic parameter of CS in 0.5 M HCl in different concentrations of inhibitor

Method	R^2	K_{ads}	ΔG_{ads}^0
Weight loss	0.9994	7.3368	−16.62
Potentiodynamic polarization	0.9949	23.419	−25.34
EIS	0.9981	15.773	−24.35

ΔG_{ads}^0, which has a negative value, indicates that the process of adsorption spontaneously occurs [26]. Generally, ΔG_{ads}^0 values below −20 kJ/mol indicate the interaction of electrostatic (physisorption) between BT and the CS surface [27]. While the ΔG_{ads}^0 a value lower than −40 kJ/mol shows chemisorption between the molecules of the inhibitor and the surface of the metal [28].

SEM-EDX Studies

An SEM-EDX spectroscopy study was conducted to see the CS surface changes of the morphology when the corrosion occurred. The CS specimen was scanned after a potentiodynamic polarization study was conducted. Fig. 6(a) shows the morphology of pure CS without treatment. The CS surface was damaged because CS came into contact with 0.5 M HCl (Fig. 6). The surface of the CS became smoother and more uniform after adding the BT inhibitor (Fig. 6(c)). The CS surface becomes very rough when the SS surface is in contact with 0.5 M HCl and the presence of oxygen (Fig. 6(d)). This result is consistent with previous research [29].

The sample composition from the EDX analysis can be seen in Table 6. There is an improvement in the carbon composition of pure CS when immersed in a corrosive medium. The composition of carbon and oxygen decreases again when there is an addition of inhibitors, but the composition of carbon increases when

Table 6. The Sample composition from the EDX

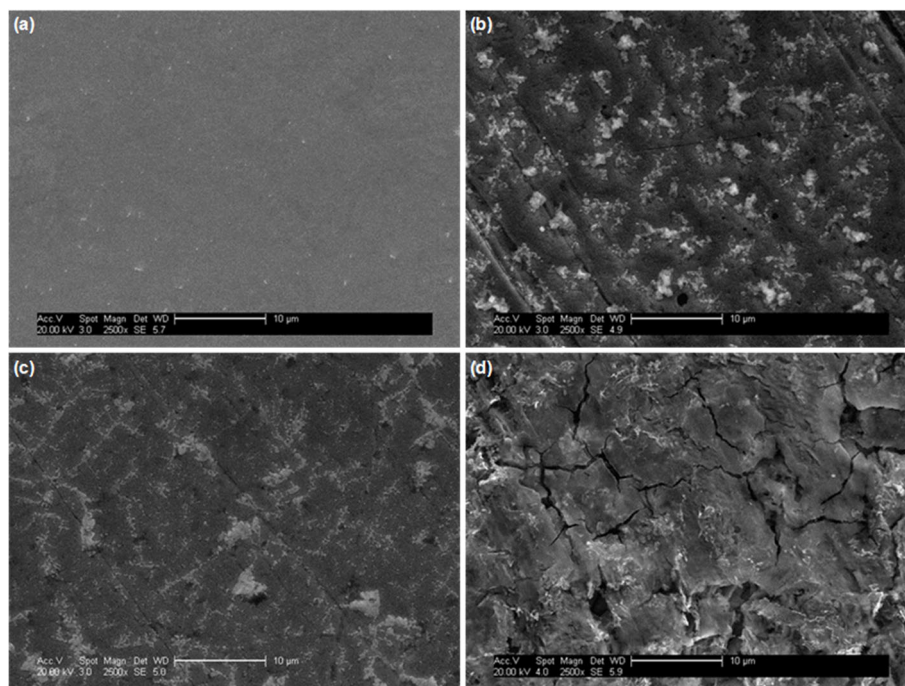|	Metal composition (%)								
	C	O	Al	Si	S	Cl	Mn	Fe	Total
Pure CS	1.54	0.88	0.19	0.59	0.45	-	1.01	97.57	100
Pure CS in HCl 0.5 M	14.93	13.78	0.26	0.33	0.28	0.38	1.28	68.76	100
Pure CS in HCl 0.5 M and 0.15 g/L inhibitor	10.98	7.86	0.19	0.63	0.52	0.51	1.74	77.57	100
Pure CS in HCl 0.5 M and 0.15 g/L inhibitor with oxygen contamination	19.11	26.82	0.25	0.66	0.43	0.78	1.34	50.61	100

Fig 6. The morphology images of (a) pure CS, (b) pure CS treated with HCl 0.5 M, (c) pure CS treated with HCl 0.5 M and 150 ppm inhibitor, and (d) pure CS treated with HCl 0.5 M and inhibitor and oxygen contamination
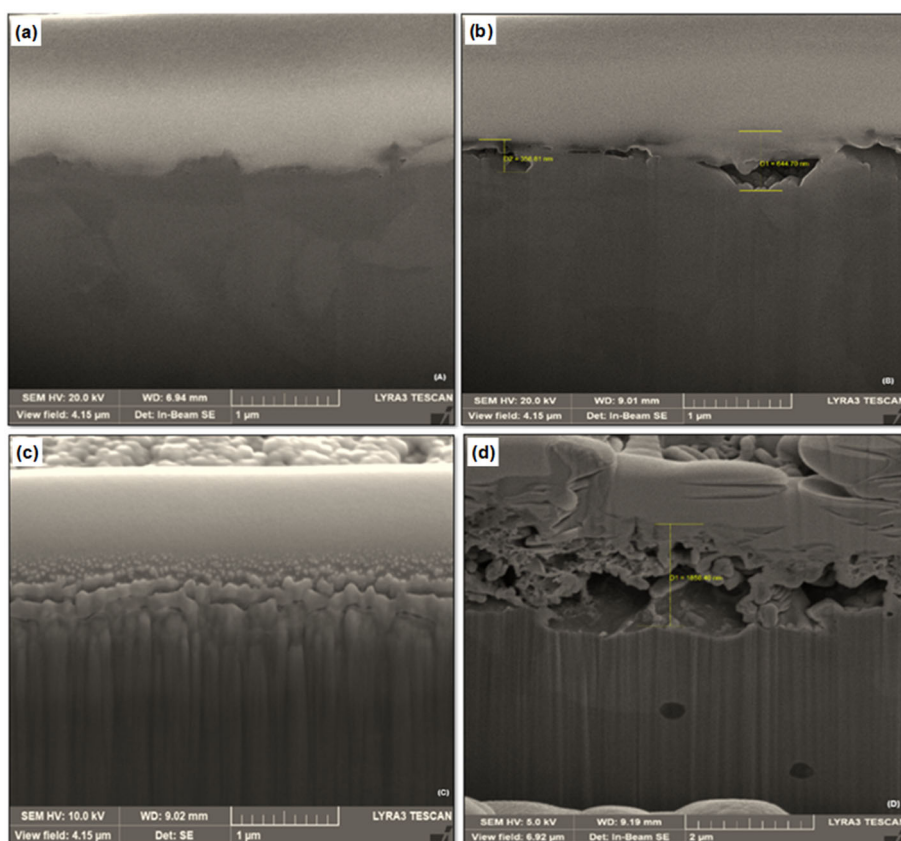

Fig 7. The FIB micrograph of (a) pure CS, (b) CS in HCl 0.5 M medium, (c) CS in 0.5 M HCl solution and inhibitor, and (d) CS in 0.5 M HCl solution and inhibitor with oxygen contamination 0.1 L/min

there is oxygen contamination. The same trend was found for the composition of Fe; the more corroded CS would decrease the composition of Fe. The lowest Fe composition was found in pure CS soaked in 0.5 M HCl, inhibitor, and O_2.

FIB Studies

The purpose of using the FIB is to observe the effect of adding inhibitors and the oxygen effect on the CS surface samples after cross-sections of the metal material are analyzed. Fig. 7 describes the FIB result of metal samples. The porous and significantly thinned zone on the surface cross-section was observed under the Pt protective layer. Fig. 7(a-d) describes the observations of cross-sectional from the four CS under different conditions. There is a layer loss from the metal that is not given an inhibitor of 300–400 nm (7(b)) compared to the metal that is given an inhibitor (7(c)). As seen in Fig. 7(c), the presence of an inhibitor can be used as a surface protective medium. However, when the metal is exposed to oxygen (7(d)), the loss of the coating due to corrosion attack becomes more apparent.

It supports corrosion attack as measured using SEM. The presence of small amounts of dissolved oxygen in water increased the overall rate of CS corrosion, and this can result in severe damage to CS. These results follow previous research that the presence of oxygen and CO_2 contaminants can increase the corrosion attack on the weldment [30].

■ **CONCLUSION**

The BT extract showed effective corrosion inhibition for CS in a 0.5 M HCl medium. The maximum %IE is demonstrated by the inhibitor concentration of 0.20 g/L by measuring weight loss (%IE 84.70). However, when the BT concentration exceeds 0.20 g/L, the percentage of inhibitory efficiency tends to decrease. The results of %IE weight loss measurements (%IE 84.70) are supported by polarization potentiodynamic (%IE 70.00) and EIS measurements (%IE 72.80). The presence of oxygen contamination reduced the %IE value in all studies. This phenomenon may be because of the inhibitors' desorption back to the bulk solution. The inhibitor concentration increased then the Nyquist plot

diameter in the EIS tended to increase (the resistance growth). On the surface of CS, a thin layer probably became the primary reason. The inhibitor adsorption process onto the CS surface is well suited to the adsorption isotherm of Langmuir. ΔG^0_{ads} which has a negative value, underlining that the adsorption process occurs spontaneously. Physisorption may occur due to electrostatic interaction with the CS surface and inhibitors. SEM and FIB showed that the effect of oxygen contamination increases corrosion damage.

■ **AUTHOR CONTRIBUTIONS**

All authors contributed evenly to this project. Meyliana Wulandari, Zahratussaadah, Nofrizal, and Andreas performed the experiment and calculations, and wrote and revised the manuscript. Pandian Bothi Raja is proofreading this manuscript.

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