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Pineapple Stem Extract (Bromelain) as Corrosion Inhibitor for Low Carbon Steel in Ambient Environment

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Abstract: Low carbon steel is an iron-based alloy with a carbon content of up to 2% (with a higher carbon content, the material is called cast iron) and is widely used for infrastructure construction. Due to the excessive use of acids, metal corrosion has become a big concern in many industries, infrastructure and public services such as water and sewage supply. Chemical inhibitors are used in a variety of ways to reduce the pace at which corrosion occurs. Inorganic substances such as phosphate, chromates, and arsenates, which are commonly used in the process industry as corrosion inhibitors to reduce corrosion of low carbon steel, have a significant disadvantage due to their toxicity. On the other hand, pineapple is a biodegradable fruit that contains no toxic chemicals and thus does not harm the environment. The adsorption of bromelain on a low carbon steel surface explains its inhibitory action in the studied. The presence of molecules with a strong affinity for metal surfaces naturally results in compounds with high inhibition efficiency and low environmental harm. The objectives of this study were to characterize the chemical and physical properties of pineapple stem extract (powder form) using FTIR, to compare the morphology for the low carbon steel surface in the presenceand without inhibitor using SEM-EDX and lastly to study corrosion inhibition efficiency of pineapple extract (Bromelain) for low carbon steel in ambient environment using weight loss and Raman Laser spectroscopy. Corrosion inhibition of mild steel in HCl by pineapple stem extract (bromelain) was studied using weight loss analysis. The inhibition efficiency increases with increase in the extract concentration. The mechanism of chemical adsorption is proposed from the observation of FTIR. Mainly, this paper discussed about the inhibitive effects of a new corrosion inhibitor as a follow-up to the research for an effective corrosion inhibitor.

Keywords: Low Carbon Steel, Corrosion, Pineapple, Bromelain, Weight Loss Measurement, Ananas Comosus

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1. Introduction

Corrosion is known as atmospheric oxidation of metals, which occurs when oxygen reacts with the metal to generate a new layer that can be harmful or beneficial. Metal's mechanical properties might deteriorate due to corrosion. It is referred to as rusting in the case of iron and tarnishing in the case of steel [1]. As the higher the corrosion rate, the more damage to its infrastructure especially the iron industry. Low carbon steel is an iron-based alloy with a carbon content of up to 2% (with a higher carbon content, the material is called cast iron) and is widely used for infrastructure construction. According to Yurt A, corrosion is the degradation or destruction of metals and alloys in the presence of an atmosphere by chemical or electrochemical means. Corrosive or aggressive medium is refers to the environment in which the metal corrodes, whereas corrosion materials are chemical solutions that consists metal in its oxidized state [5]. Iron tends to be highly reactive with most of the atmospheric environments as because of its natural tendency to form an iron oxide. According to the carbon percentage, the categorization is further divided into three types; which are low carbon steel (less than 0.25% C), medium carbon steel (0.25% until 0.70 % C) and high carbon steel (0.70% until 1.05% C)[6]. The inhibitors in general, react with the corrosion agent that has already developed on the metal surface to produce a coherentand insoluble coating [7].

Pineapple (Ananas comosus); is a delicious tropical fruit that consists of high juice content as have a vivid tropical flavour and provides many health benefits. Meanwhile, bromelain is a group of sulphur-containing proteolytic (a protein digesting) enzymes found in the pineapple which helps with digestion system in the human body [3]. The addition of bromelain on the low carbon steel will enhance the ability of a stronger and more durable infrastructure development [4]. Inorganic substances such as phosphate, chromates, and arsenates, which are commonly used in the process industry as corrosion inhibitors to reduce corrosion of low carbon steel, have a significant disadvantage due to their toxicity. On the other hand, pineapple is a biodegradable fruit that contains no toxic chemicals and thus does not harm the environment. The adsorption of bromelain on a low carbon steel surface explains its inhibitory action in the studied. The presence of molecules with a strong affinity for metal surfaces naturally results in compounds with high inhibition efficiency and low environmental harm.

This study will review the relationship between metal (low carbon steel) and the corrosion then aiming for conceptual theoretical framework based on the corrosion inhibitor as anti-corrosion method. Synthetic organic and inorganic corrosion inhibitors are costly, and some of them can be harmful for human and the environment; therefore, they must be substituted for a normal, non-toxic and commercially viable corrosion inhibitor. Hence, the quest for a healthy and environmentally sustainable "green inhibitor" is set in motion [2].

There several objectives in this project, which were to characterize the chemical and physical properties of pineapple stem extract (power form) using Fourier Transform Infrared spectroscopy (FTIR). Next, is to compare the morphology for the low carbon steel surface in the presence and without inhibitor using Scanning Electron Microscope with Energy Dispersive X-ray analysis (SEM-EDX). Lastly, to study corrosion inhibition efficiency of pineapple extract (Bromelain) for mild steel in ambient environment using Weight loss and Raman Laser spectroscopy.

2. Methodology

This inquiry discusses the inhibitive effects of a new corrosion inhibitor as a follow-up to the research for an effective corrosion inhibitor. FTIR spectroscopy was used to evaluate the newly synthetic corrosion inhibitor, bromelain acid, which is present in pineapple stems.

2.1 Sample preparation

The corrosion inhibition behaviour on the surface of mild steel in corrosive environment was studied using weight loss techniques. The main sample preparation that will be utilized in this research is low carbonsteel (LCS). The low carbon steel coupon will be prepared in a rectangular shape withdimensions of 10.0 mm x 10.0 mm x 1.0 mm with a surface area of 10 mm^2. The extraction of bromelain from pineapple (Ananas comosus) powder will be weighed into 0.2 g, 0.4 g and 0.6 g of its extract and put into the petri dish. Then, those extraction be diluted into 100 ml beaker of 1M HCI (Hydrochloric acid). Lastly, the mixture then be kept and sealed with aluminium foil.

2.2 Analytical techniques

Analytical techniques can be defined as the method used for the qualitative andquantitative determination of concentration of a compound by using various techniques like spectroscopies, chromatography, and gravimetric analysis. Analytical techniques that will be employed to achieve the objective are Scanning Electron Microscopy- Energy Dispersive X-Ray Analysis (SEM- EDX), Fourier-transform infrared spectroscopy (FTIR), Laser Raman spectroscopy and weigh loss analysis.

3. Results and Discussions

SEM micrographs of mild steel after exposure of warm environment with the absence and presence of the inhibitor with different concentrations will get the results as shown in Figure 4.1. As shown in Figure 4.1 (a), describes the image of pure low carbon steel structure as clean structure which the coupons have been polished meanwhile Figure 4.1 (b) shows the micrograph exhibited a cocoon-like structure for low carbon steel samples with the absence of inhibitor (Ananas comosus extract or bromelain) as it undergoes a localized attack within the exposure period. Next, the surface morphology of the low carbon steel (LCS) treated with inhibitor improved as increasing concentration of inhibitor will shows clearer surface as shown in Figure 4.1 (c), Figure 4.1 (d) and Figure 4.1 (e).

According to EDX study, the increasing in the value of oxygen (O) is attribute to the formation of ferrous hydroxide, meanwhile the increasing in the value of carbon (C) is due to the inclusion of catechin (as shown in Table 4.1) which function as an active inhibitor and complexes with the mild steel surface.

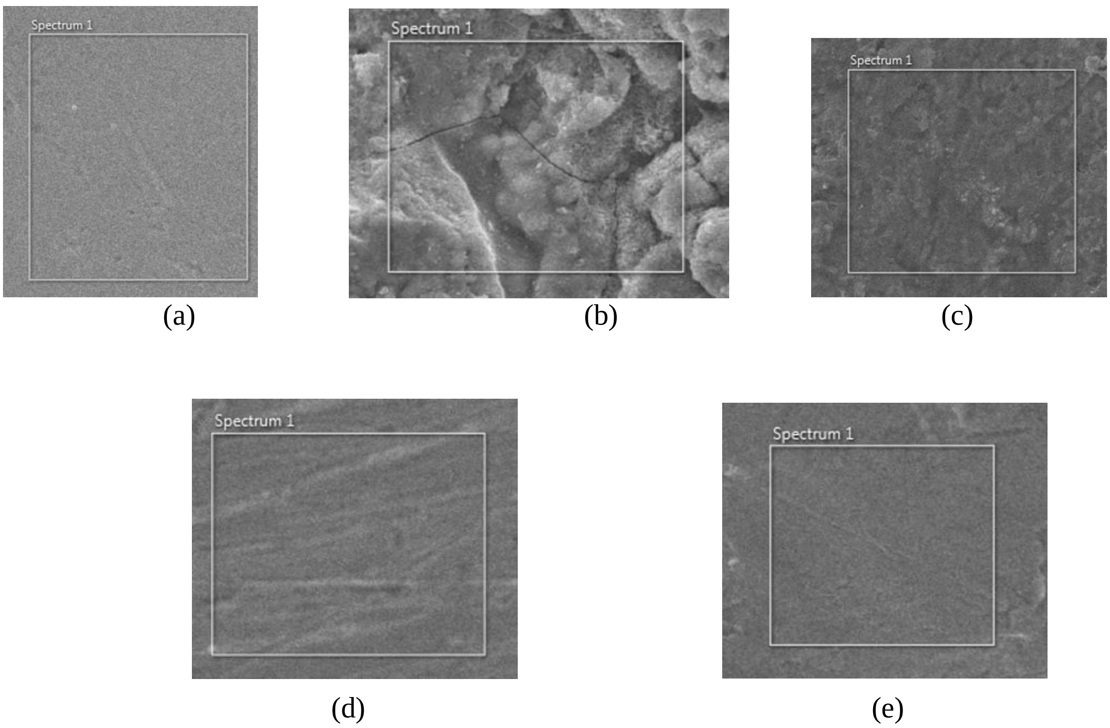
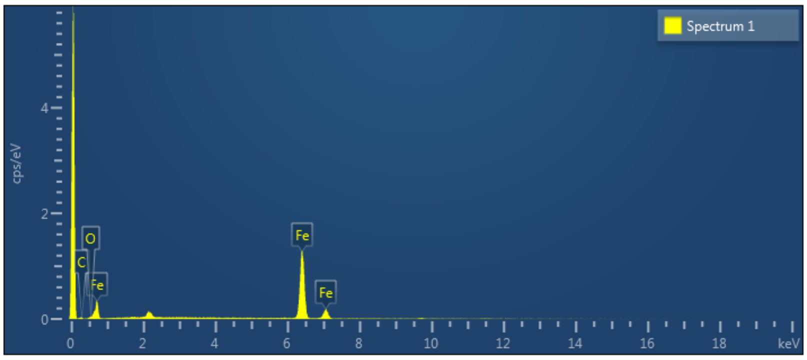


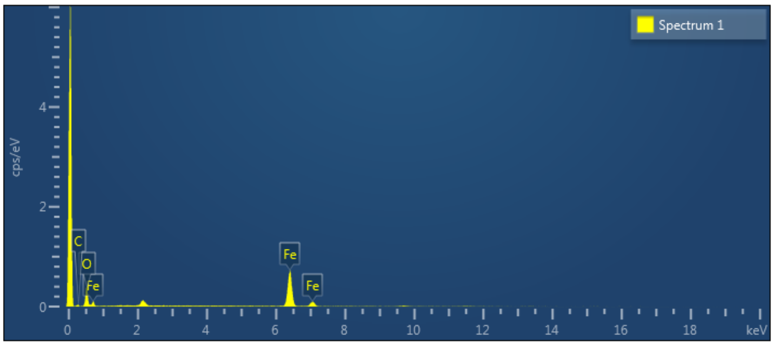
Figure 4.1: SEM micrograph of low carbon steel in (a) pure low carbon steel, (b) without inhibitor, (c) with 0.2 g/L extract inhibitor, (d) with 0.4 g/L extract inhibitor, (e) with 0.6 g/L extract inhibitor

Table 4.1: The composition of the samples regrading to the EDX analysis

Samples	Elements (%)		
	Fe	O	C
Pure low carbon steel	91.58	1.44	6.98
Low carbon steel without inhibitor	63.65	27.00	9.34
Low carbon steel with 0.2 g/L inhibitor	78.57	13.31	8.12
Low carbon steel with 0.4 g/L inhibitor	86.47	0.82	12.71
Low carbon steel with 0.6 g/L inhibitor	88.95	1.42	9.63



(a)



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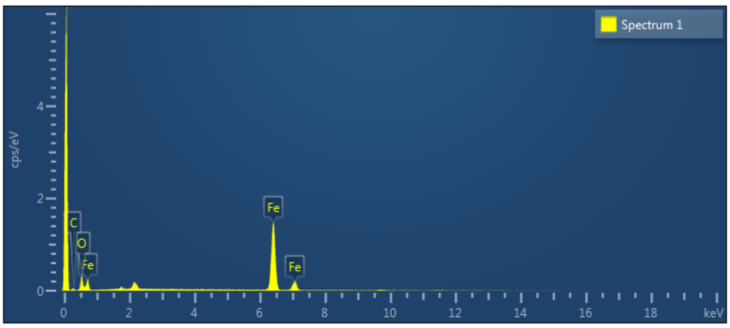
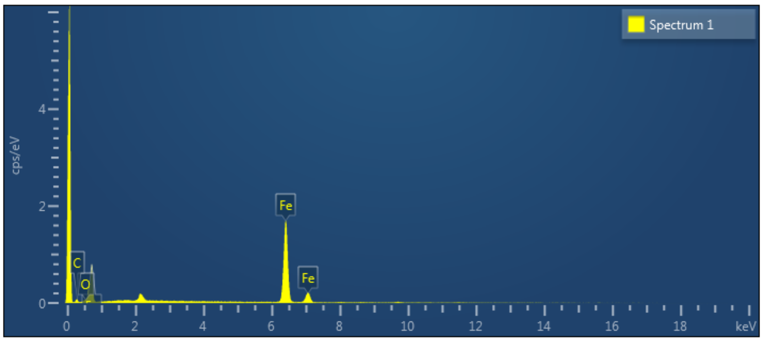


(c)



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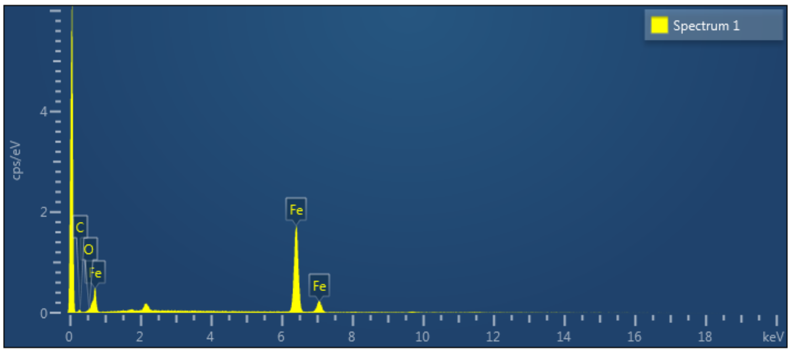


(e)

Figure 4.2: The EDX spectra of low carbon steel in (a) pure condition, (b) without inhibitor, (c) with 0.2 g\L extract inhibitor, (d) with 0.4 g\L extract inhibitor (e) with 0.6 g\L extract inhibitor

From the FTIR investigation, observed a shift in the spectra after immersing mild steel in 0.5 g/L extract diluted with distilled water solution, confirming the interaction between extract and distilled water. Because those bonds were missing from the spectra, the FTIR investigation revealed that alkynes ($\equiv C - H$) and aromatic rings ($C - C = C$) bonds were responsible for the inhibitor interaction as will be applied on low carbon steel surfaces. The alkynes bond have a strong intensity meanwhile for the aromatic ring have medium intensity.

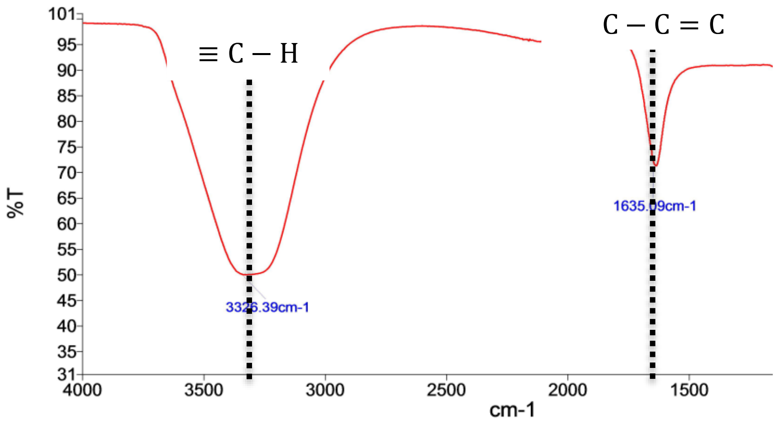


Figure 4.3: FTIR analysis from bromelain extract

The absorption of bromelain onto mild steel was also evaluated by Raman spectroscopy. For the first observation, Figure 4.4 shows the corresponding spectra for pure mild steel. It illustrates that there was several functional groups such as C-C bond (at 976.2 cm^{-1}) and CH^2 bond which is a polyethylene (at 2872.62 cm^{-1}) as the mild steel initially consists a strong bond between carbon elements.

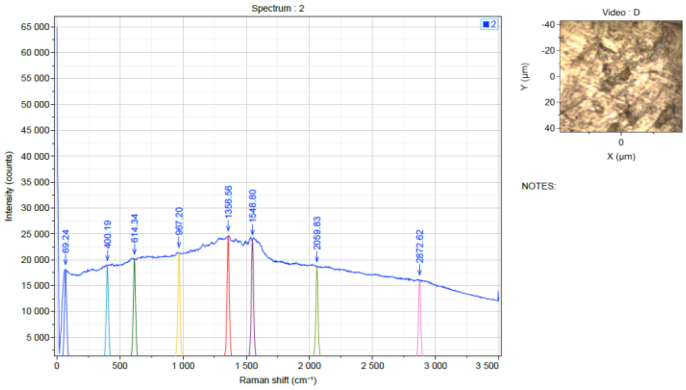


Figure 4.4: Raman spectra of low carbon steel

Figure 4.5 illustrates the corresponding spectra of mild steel sheet after exposure to a corrosive environment for a week in the absence of inhibitor. It shows there was only left the C-C bond (at 1276.45 cm^{-1}) after the exposure, as the corrosion had been happened. The surface reaction product was a red-orange color, the orange being more dominant and show rusting gives a big effect on the low carbon steel surfaces.

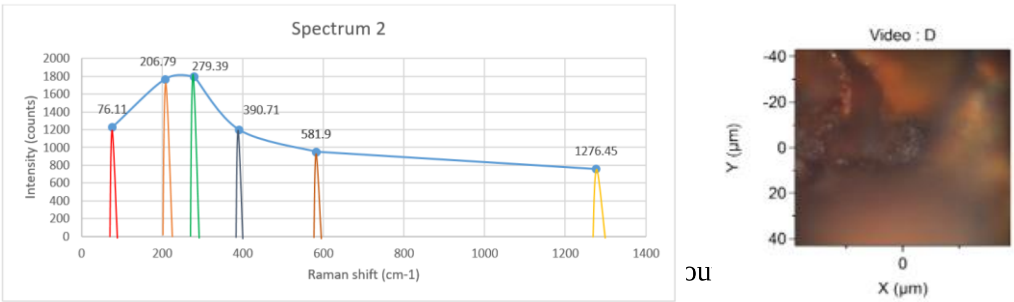
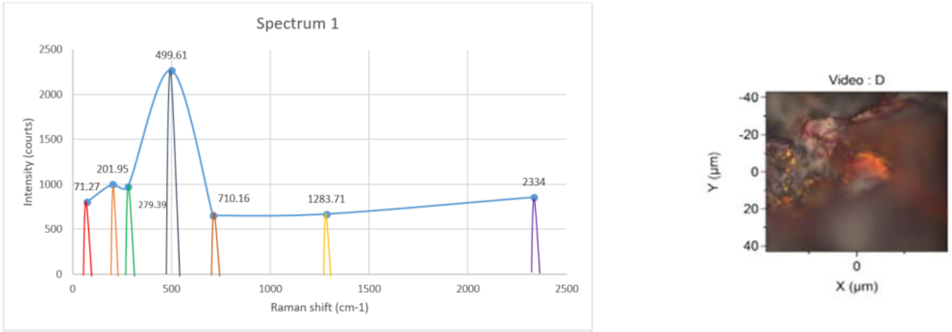
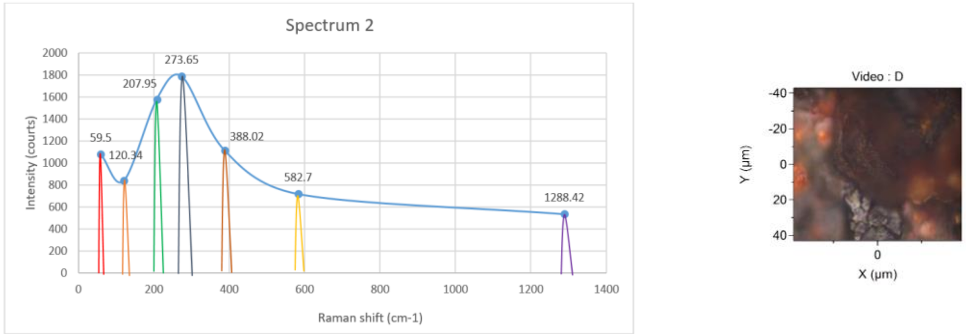


Figure 4.5: Raman spectra of low carbon steel

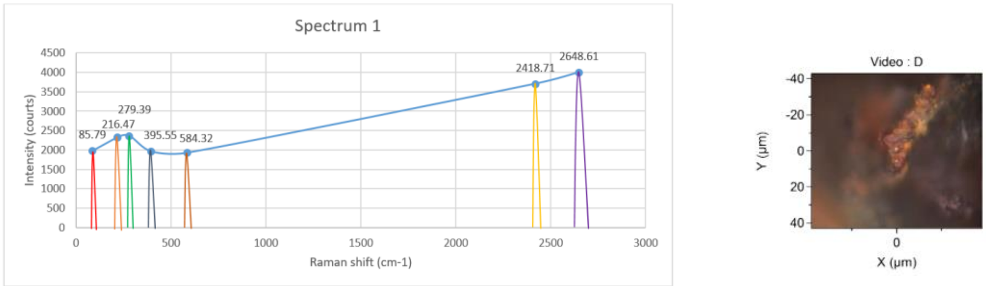
Different concentration of inhibitor which saluted onto the mild steel had been manipulated during this case study as shown in Figure 4.6 (a), Figure 4.6 (b) and Figure 4.6 (c) as all of the samples undergoes exposure in warm air environment within a week. For the Figure 4.6 (a), the mild steel been saluted with 0.2 g/L of bromelain extract. It shows the final result after the mild steel undergoes exposure, several functional groups appeared such as C-C bond (at 710.16 cm^{-1}), C=O bond (at 1283.71 cm^{-1}) which is a amide group and C=C bond (at 2334.00 cm^{-1}). Meanwhile for Figure 4.6 (b), mild steel been saluted with 0.4 g/L of bromelain extract. It illustrates that after the mild steel undergoes exposure, the C-C bond (at 1288.42 cm^{-1}) keep been restored. The surface of mild steel seems better as lesser surface damaged. Next, for Figure 4.6 (c); the mild steel been saluted with 0.6 g\L of bromelain extract. It shows that the outcome after mild steel undergoes the exposure, observed that the C-C bond is present at 584.32 cm^{-1}. Figure 4.7 illustrates the different among all sample in its Raman spectra analysis. It seems that the spectra's characteristics indicate that bromelain coating was effectively adsorbed on the mild steel surface, and the best inhibitor condition was formed as a result.



(a)



(b)



(c)

Figure 4.6: Raman spectra for low carbon steel with; (a) 0.2 g/L inhibitor, (b) 0.4 g/L inhibitor, (c) 0.6 g/L inhibitor

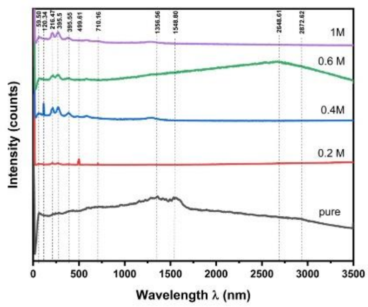


Figure 4.7: Raman spectra for low carbon steel with various conditions

As figure 4.8 shown, the differences of the condition gives the expected outcomes. The initial condition of the pure mild steel (sample a) shows its surface as shines which has been polished before the exposure. The mild steel which have been exposed without inhibitor (sample b) gives an image of it damaged and lot of rust appears on it. As for sample c, sample d and sample e, those shows the higher concentration of its inhibitor the lesser the mild steel being damaged. As the result, sample e shows the effectiveness of the inhibitor in avoiding the mild steel being rust after been exposed within a week of exposure.

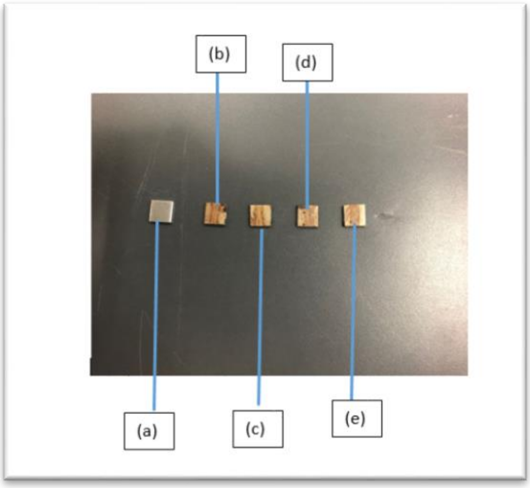


Figure 4.8: Low carbon steel conditions after exposure in (a) pure condition, (b) without inhibitor, (c) with 0.2 g\L extract inhibitor, (d) with 0.4 g\L extract inhibitor, (e) with 0.6 g\L extract inhibitor

In determining the activation parameter of corrosion process, the corrosion rate (CR) and Inhibition efficiency (IE) was used. As result, the Table 4.3 was completed as the data observed during the weight loss being calculated.

Table 4.3: Corrosion parameter for low carbon steel in 1M HCI in absence and presence of the bromelain extract from weight loss measurement

Sample	Weight (g)	Corrosion rate (mg cm^{-2} h^{-1})	Inhibition efficiency (%)
Pure low carbon steel	0.855	-	-
Low carbon steel without inhibitor	0.823	0.1333	-
Low carbon steel with 0.2 g/L extract	0.838	0.0708	46.9
Low carbon steel with 0.4 g/L extract	0.845	0.0417	68.7
Mild steel with 0.6 g/L extract	0.848	0.0292	78.1

4. Conclusions

(Bromelain) contains several simple to complex phytochemicals that can be adsorb effectively over the metal (low carbon steel) surface studied and build protective shields in avoiding corrosion. The phenomenon of chemical adsorption on the studied low carbon steel is proposed from the trend of increase in inhibition efficiency with increase in concentration of its inhibitor. 0.6 g/L of bromelain extraction is the good concentration of coating onto the low carbon steel surfaces as highly preventing the samples from rusting. The study of pineapple extract (Bromelain) acts as an excellent inhibitor for low carbon steel corrosion in ambient environment. The results obtained from weight loss studies show that inhibition efficiency increases with the increasing surfactant concentration as the pineapple stem extract.

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