Malaysian Journal of Chemistry, 2019, Vol. 21 (2), 64-70
(Special Issue: *5th Intl. Conf. on Oils and Fats 2018*, Universiti Kebangsaan Malaysia)

Temperature Effects toward Corrosion Rate of Carbon and Mild Steel Using Red Palm Oil as Natural Corrosion Inhibitor†

M. Ili Afiqah, Yusri Zulkafli, Norinsan Kamil Othman, Azwan Lazim, Wan Nur Aini Wan Mokhtar and Mohd Firdaus Mohd Yusoff*
Centre for Advanced Materials and Renewable Resources
Faculty of Science and Technology,
Universiti Kebangsaan Malaysia, Selangor, Malaysia
*Corresponding author (e-mail: fir_my@ukm.edu.my)

Red palm oil was studied as a corrosion inhibitor for mild and carbon steel in an acidic medium at different temperatures. It was shown that the steel weight loss was directly proportional to the increase of temperature. Mild steel lost about 1.34 mg of weight at 25°C and reached a maximum weight loss at 60°C was 2.41 mg. Carbon steel underwent about 1.41 mg weight loss (25°C) until 2.47 mg (60°C). The rate of corrosion was also increased as the temperature increased. The maximum corrosion rate for both mild and carbon steel at 60°C was 15.71 mpy and 16.10 mpy, respectively. The maximum rate of corrosion inhibitor efficiency for mild and carbon steel was found to be 91.1% and 80.1% at 25°C. The percentage of corrosion inhibitor efficiency gradually decreased when the temperature increased. SEM-EDX results showed both surfaces of mild and carbon steel were smoothed and no holes at 25°C. However, at 60°C corrosion effect occurred on the surface of both types of steel. Based on the percentage of chlorine, oxygen, and ferum atom mass, the oxidation and corrosion impacts were lower for mild steel compared to carbon steel.

Keywords: Red palm oil; natural corrosion inhibitor; temperature; steel

Received: July 2018; Accepted: April 2019

Corrosion is defined as a failure, damage, decline or degradation of metal due to the occurrence of redox reactions between metal and oxygen. In simple words, corrosion means the damage of material due to the mutual chemical reaction between the environment and the material itself. The corrosion of steel brings a huge impact on the country's economic growth, especially in industries such as oil and gas [1]. Steel is easily exposed to corrosion because there is 98.7% of the iron in the composition. When exposed to air, iron will react with oxygen molecule hence forming iron (III) oxide. Although this corrosion phenomenon is unstoppable, it can still be controlled.

Realizing the importance of controlling the corrosion problems, few methods have been successfully developed, among them are by coating of the metal with polymer [2] and protection of anode/cathode by using inorganic inhibitors [3]. Corrosion controlling method using corrosion inhibitors are the most commonly studied method as compared to the coating of the metal method [4]. Nevertheless, these methods have weaknesses in which the metal coating will induce the risk of damaging the metal while the protection of anode/cathode by using inorganic inhibitors will contribute to the increase of non-treated toxic waste, especially into the aquatic resources. This condition will expose the aquatic life to hazardous contamination. Also, people who use the river as the main source for drinking water will be exposed to a variety of dangerous diseases [5].

Inhibitors are the substances that are added on the surface of the metal at a low concentration to delay the rate of rusting. This process is done by increasing the anodic or cathodic polarity as well as electrical resistance of the metal surface and decreasing the movement or adsorption of ion. Corrosion inhibitors are substances that are added into the corrosive media in a small quantity that will either lower or prevent the reaction between the metal and the media from happening. Corrosion inhibitors are widely used in industries such as cooling system, production of oil and gas, and many more [6].

Corrosion inhibitors involve physical or chemical adsorption and can cause the disturbance of cathodic or anodic on the surface of the metal. Sometimes, both reactions will occur on the adsorption site. The effectiveness of corrosion inhibitor depends on the degree of adsorption that is determined by size, shape, orientation, and molecule electrical charge [7].

†Paper presented at the *5th International Conference on Oils and Fats 2018* (SMILE2018), 14-15 August 2018, Universiti Kebangsaan Malaysia

Red palm oil is used in this research because it has the potential to be applied as a corrosion inhibitor due to the presence of various components with different functional groups. Major components in red palm oil are oleic acid (18%), palmitic acid (16%), stigmasterol (11%), nonadecene (10%), octadecanoic acid (6%), tetracosahexane (2%), campesterol (1.5%), cyclopentane (0.73%), tricosene (0.35%), cyclooctatetraene (0.33%), and free fatty acid (0.33%) [8]. The reactivity of the different functional group will increase the adsorption of red palm oil on the surface of the metal. This statement is emphasized by El-Etre[9], stating that large molecular structure, double bonds, centres, and reactive groups are important characteristics to produce a high-quality corrosion inhibitor. In this research, by using temperature as the rusting factor, the effectiveness of red palm oil as an organic inhibitor was tested for corrosion on metal steel and soft metal at different temperature.

MATERIALS AND METHODS

Sample

Materials used in this research are red palm oil, *n*-heptane, hydrochloric acid, acetone, carbon steel, soft steel, and distilled water.

Red Palm Oil Composition Analysis

Gas chromatography-mass spectroscopy (GC-MS). GC-MS is one of the techniques to analyse volatile compounds. GC-MS is usually used to separate compound or sample into smaller molecule component and has two main parts which are gas chromatography (GC) and mass spectrometer (MS). Smaller molecule components or charged fragments are then qualitatively analysed by using MS that will produce a spectrum through the detection of various charged fragments.

Red palm oil is a non-volatile compound and needs to be changed into fatty acid methyl ester to decrease the boiling point. The injection temperature that is used is over 200°C, with the presence of inert gases.

Fourier-transform Infrared Spectroscopy

Fourier transformation infrared (FTIR) spectroscopy analysis was done to identify the functional group that was present in the studied material. In this research, the composition of red palm oil was identified by using FTIR at the wave range of 400 to 4000 cm^{-1}.

Analysis and Characterisation of Carbon Steel and Soft Steel

Steel inhibition test. The implementation of this research was based on the standards set by the *American Society for Testing and Materials (ASTM)* that is *ASTM G31-1972*. Carbon steel SAE 1045 (composition of 0.45% C, 0.75% Mn, 0.04% P, 0.05% S and 98.71% Fe) and soft steel AISI 1020 (composition of 0.45% Mn, 0.20 % C and 99.10% Fe) were cut into round-shape with the size of 3.0 mm and 1.63 cm diameter length by using the cutting machine. Illusion cord was tied on every steel for each suspension in the acidic medium. Every carbon steel and soft steel were smoothened by a graded sandpaper to eliminate any sludge, contaminants, and oxide film on every surface of the steel. The steel was then de-greased by using acetone to eliminate any grease, dirt, or dust on the surface of the steel to reduce any error throughout the research. The steel was soaked in the ultrasonic bath for 3 minutes to eliminate any leftover grease, dirt or dust trapped on the surface of the steel. A cold-mode dryer was used to dry the steel. The weight of the steel was measured before immersing it into the inhibitor solution for 5 hours at different temperatures of 25, 30, 40, 50, and 60°C. After 5 hours, the steel was removed from the inhibitor solution, dried and weighed. The inhibition efficiency was determined by measuring the mass loss of the steel.

Mass loss test. The mass loss of carbon and soft steel is the measurement for the physical rate of corrosion. According to Obi-Egbedi *et al.* [10], although this technique is simple, it is believed that it could observe the inhibition efficiency well. The carbon steel and soft steel were immersed in the flask containing a solution mixture of 1 M HCl which acted as the corrosive media, *n*-heptane as the solvent, acetone as co-solvent and red palm oil as a raw material in the production of the corrosion inhibitor solution. The mass loss of carbon steel and soft steel was measured in milligrams based on the equation below:

$$B = (B_i — B_f) \text{ mg} \quad (1)$$

where, B = mass loss of steel; B_i = original mass of steel; and B_f = final mass of steel.

The inhibition efficiency (% IE) for red palm oil (RPO) as the corrosion inhibitor is as below:

$$\% \text{ IE} = (1 - w_1 / w_2) \times 100 \quad (2)$$

where, w_1 and w_2 is the mass loss of carbon steel and soft steel with or without the presence of inhibitors.

Kinetic test for the corrosion of carbon steel and soft steel. The kinetic test of corrosion for both types of steel was determined by the equation below:

$$CR \text{ (mpy)} = 534W/ DAT \quad (3)$$

where, W is the mass loss, D is the density of inner steel coupons in the unit of gram/cm^3, A is the area the unit of cm^2, and T is the immersion time in the unit of an hour.

Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM-EDX**)**

SEM-EDX is used to scan the surface of the sample by using a focused electron beam. SEM is used to show the condition of the surface of the sample, while EDX is used to identify the presence of elements on the surface of the sample. In this research, SEM-EDX was used to characterise the surface of the carbon steel and soft steel after being immersed in the corrosion inhibition solution for 5 hours at different temperatures from 25, 30, 40, 50 to 60°C.

RESULTS AND DISCUSSION

Fourier-transform Infrared Spectroscopy (FTIR)

Based on the RPO FTIR spectrum shown in Figure 1, the main composition of RPO consists of the ester functional group (-COOR). This is due to at the peak of 1744 cm^{-1} and 1098 – 1238 cm^{-1}, respective peaks showed the strained bond of C=O and C-O in the functional group of –COOR. Besides, the peak at 1655 cm^{-1} showed the presence of C=C strain bond. At the peak of 2853 – 3008 cm^{-1}, the spectrum showed the presence of a weak spectrum where it is a curve for the strain of C-H bond in the alkyl chain. The known spectrum in this analysis is the peak for a functional group of carboxyl (C=O), methyl group (CH_3) and carbon double bond (C=C). These functional groups have the potential to inhibit the corrosion process. According to Abiola and Oforka [11], organic mixture such as hydroxyl (-OH), methoxyl (-OCH_3) and the methyl (-CH_3) are known as electron donor group that plays an important role in the inhibition of metal corrosion in acidic media. This mixture will be adsorbed on the surface of the metal and then reduce the area of the surface of the metal that is exposed to the attack of acidic media [12].

Gas Chromatography Mass Spectroscopy (GC-MS)

Based on the chromatogram in Figure 2, there are 4 peaks which are identified as peaks 1, 5, 6, and 8. Peak 1 with the retention time of 19.32 minutes is methyl palmitate, while peak 5 which consists of 3 peaks is methyl oleate. Peak 6 (retention time: 26.26 minutes) and peak 8 (27.76 minutes) are methyl linoleate and methyl linolenate respectively [13]. The same result is obtained and reported in the research done by Abdulkarim *et al.* [14].

Effect of Temperature on Mass Loss and Rate of Corrosion

Table 1 shows the mass loss and the rate of corrosion of carbon steel and soft carbon at a different temperature where mass loss and rate of corrosion is directly proportional to the increase in temperature. From the observation, the rate of corrosion for carbon steel is higher than soft steel. However, both types of steel reached a maximum rate of 15.71 mpy and 16.1 mpy at 60°C respectively.

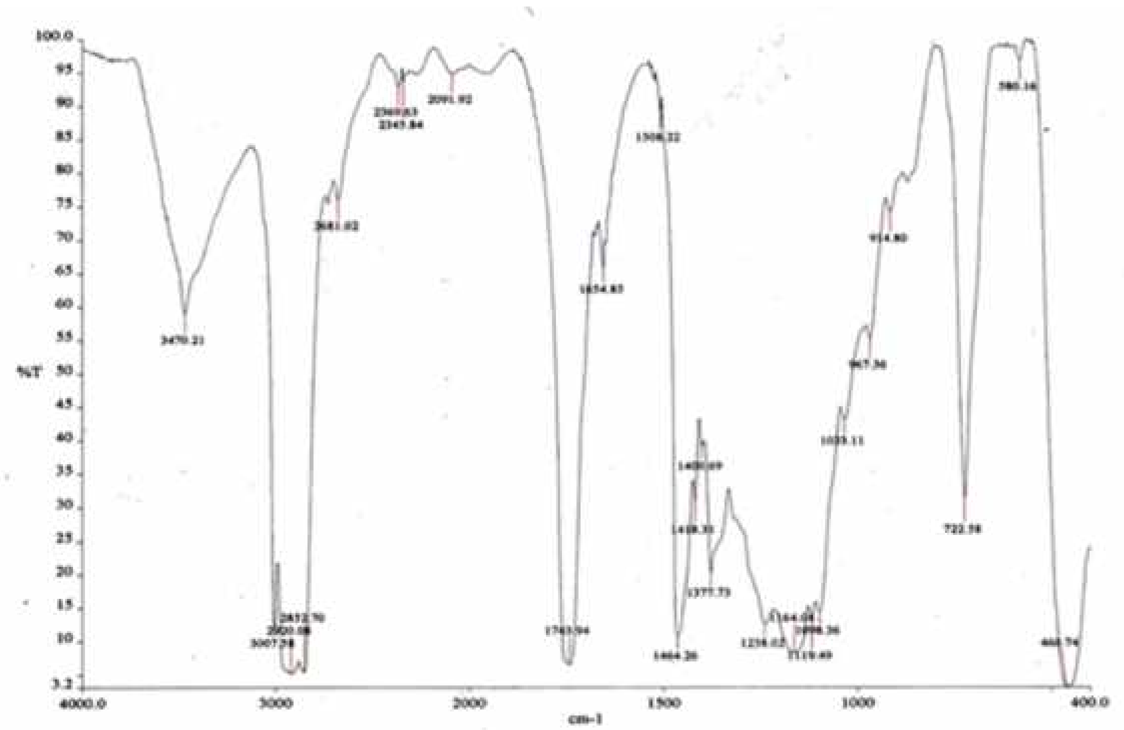

Figure 1. FTIR spectrum for red palm oil.

Table 1. Mass loss and rate of corrosion of soft steel and carbon steel at different temperature.

Type of steel	Temperature(°C)	Mass loss (mg)	Rate of Corrosion (mpy)
Soft Steel	25	1.34	8.74
	30	1.58	10.30
	40	1.79	11.67
	50	1.87	12.19
	60	2.41	15.71
Carbon Steel	25	1.41	9.19
	30	1.85	12.06
	40	2.18	14.21
	50	2.27	14.80
	60	2.47	16.10

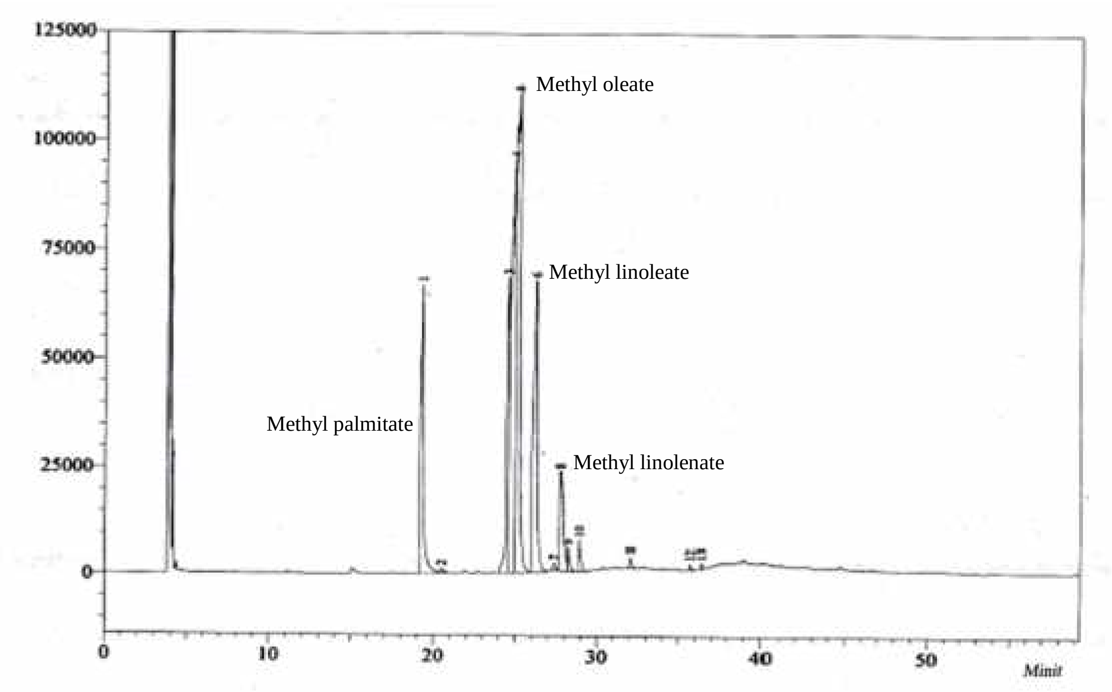

Figure 2. GC chromatogram of red palm oil.

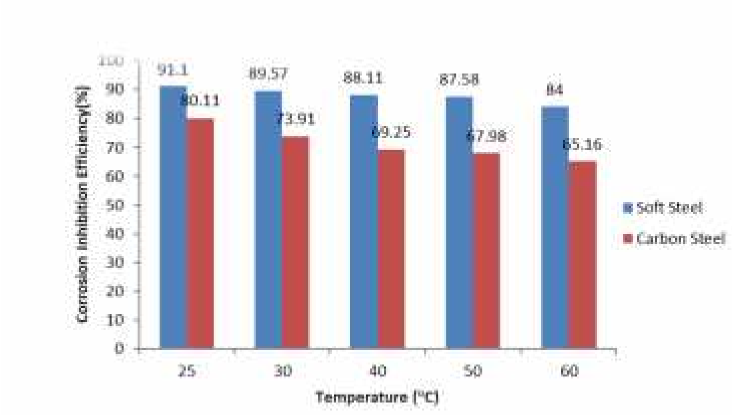

Figure 3. Percentage graph of RPO corrosion inhibitor efficiency (mg) at different temperatures (°C).

Effect of Temperature on Corrosion Inhibition Efficiency

Figure 3 shows the increase in the percentage of corrosion inhibition efficiency for both types of steel. Overall, both are found to be parallel to the increase in temperature from 25°C to 60°C. The efficiency improvement pattern confirmed that the inhibitor that was used to inhibit corrosion through the chemical adsorption mechanism. The effect of temperature on the reaction of acid-metal inhibited was very complex. This was due to the changes that occurred on the surface of the metal, such as sudden outbursts and inhibitor deposition. The inhibitor used might experience decomposition or/and re-arrangement of the molecule.

Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy (SEM-EDX)

Figure 4 shows the morphology on the surface of soft and carbon steel after being immersed in acidic medium (1.0 M) at the temperature range of 25-60°C for 5 hours with the presence of inhibitors. Figures 4(a) and 4(c) are the result of the surface of the soft steel and carbon steel that was immersed in the corrosion inhibition solution at the temperature of 25°C. Both surfaces of the steel were smooth and covered by a thin film. This result was supported by EDX spectrum obtained at the temperature shown in Figures 5(a) and 5(c). Spectrum 5(a) shows the weight percentage for the chlorine atom; oxygen and iron in soft steels are 0.70, 18.97 and 62.03%, respectively. In spectrum 5(c), the weight percentage for chlorine atom, oxygen and iron in carbon steels are 0.11, 18.15, and 56.96% respectively.

Figures 4(b) and 4(d) shows the surface of the soft steel and carbon steel that was inhibited at the temperature of 60°C. This result showed the formation of lumps on the surface of the steel caused by the heating that accelerated the oxidation reaction. To support this statement, the result of the EDX spectrum in figures 5(b) and 5(d) show the weight percentage for chlorine atom, oxygen, and iron in soft steel which are 1.92, 34.88, and 38.86%, respectively.

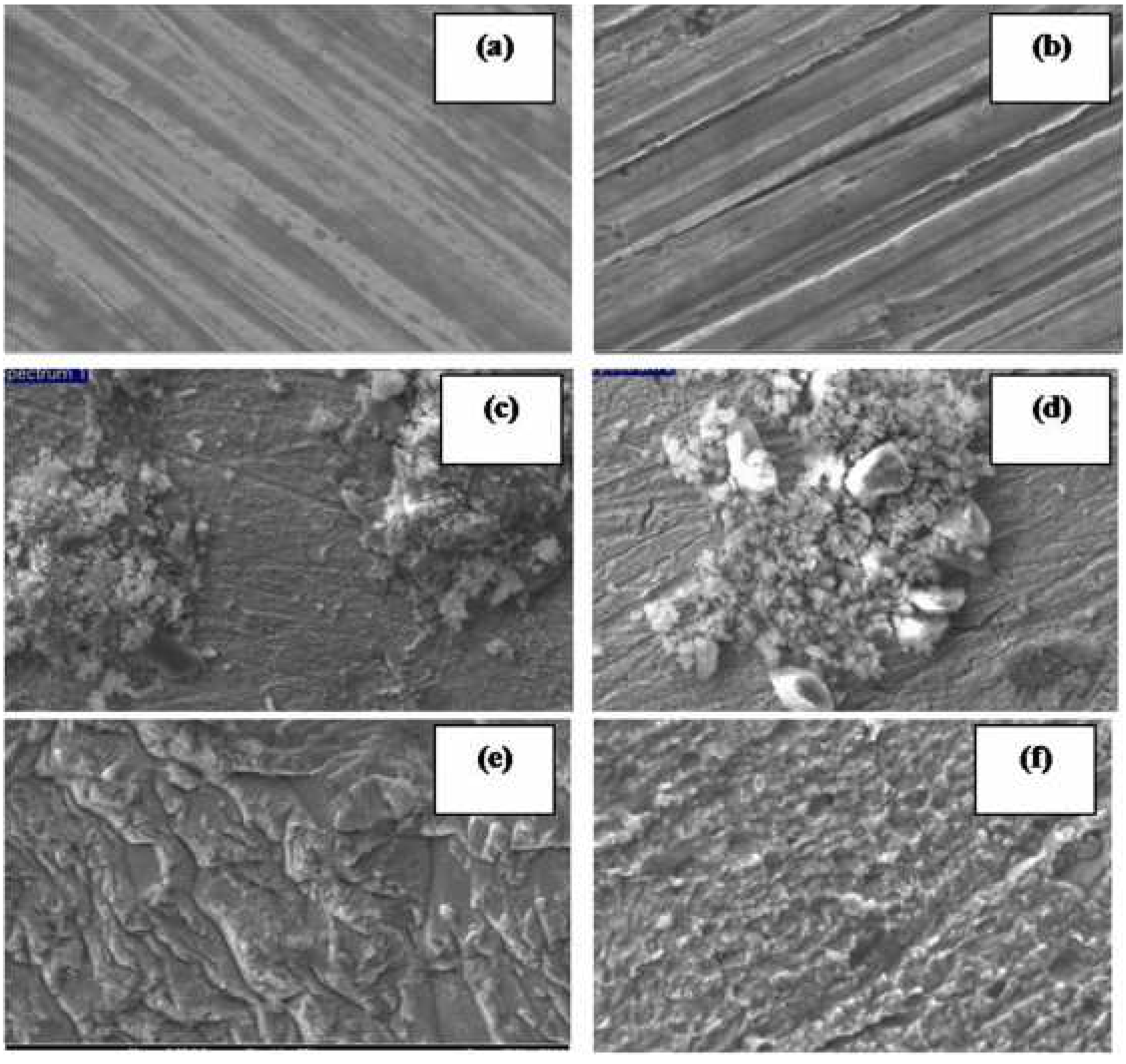

Figure 4. Morphology of the surfaces of soft steel and carbon steel that are immersed at the temperature of 25°C that is (a) and (c), and at a temperature of 60°C that is (b) and (d). While, (e) and (f) are the surface of the soft steel and carbon steel that are immersed in empty solution (a mixture of HCl and *n*-heptane).

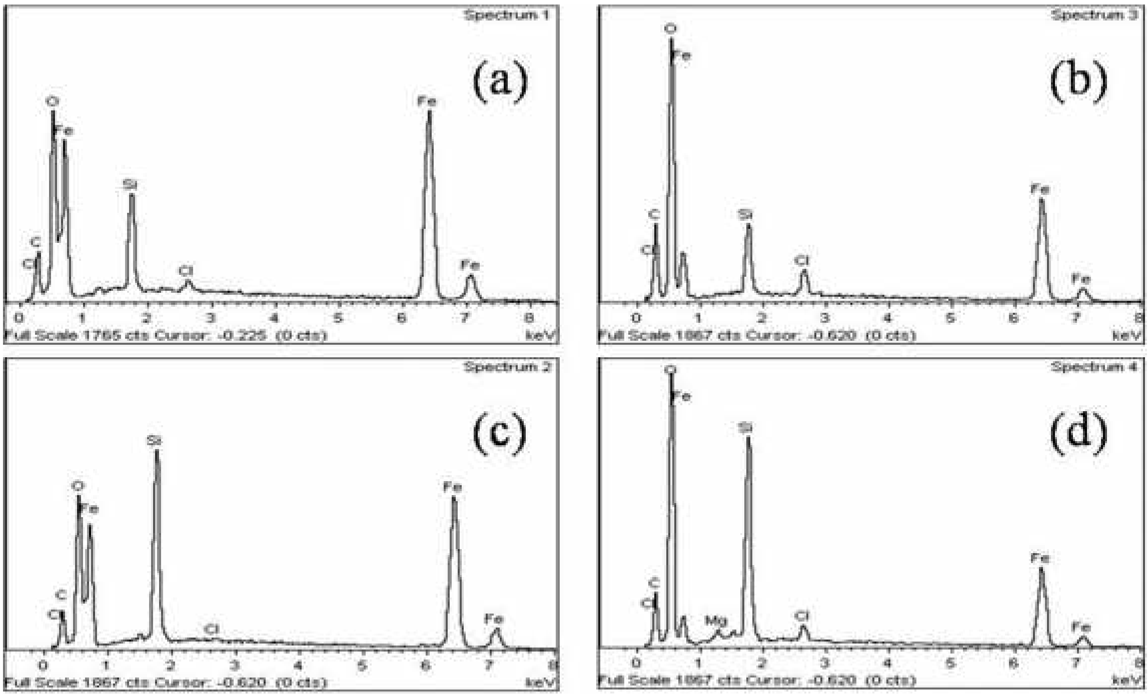

Figure 5. EDX spectrum of soft steel and carbon steel that are immersed at the temperature of 25°C that is (a) and (c), and at the temperature of 60°C that is (b) and (d).

The spectrum in figure 5(d) shows the percentage of a chlorine atom, oxygen, and iron in carbon steel which is 1.22, 37.75 and 30.30% respectively.

Besides, both types of steel experienced a decline of iron atom weight percentage and the increase in the percentage weight of chlorine and oxygen atom when the temperature was increased. The increase in the percentage of the oxygen atom and the decrease in iron atom percentage were caused by the oxidation reaction that occurred during the heating. Increase in percentage weight of chlorine was caused by the attack of the surface of the steel by the acid.

CONCLUSION

Red palm oil reacted more efficiently to inhibit the corrosion of soft steel with the corrosion inhibition efficiency reaching 91.1% as compared to other corrosion inhibitors. Moreover, it does not react selectively towards the surface of certain metal and could be applied to both of soft and carbon steel types.

ACKNOWLEDGEMENT

We would like to express our highest gratitude to all laboratory staff in the Department of Chemistry, Faculty of Science and Technology, and National University of Malaysia, for the support, help, and guidance throughout the laboratory sessions.

REFERENCES

1. Osokogwu, U. and Oghenekoro, E. (2012) Evaluation of corrosion inhibitors effectiveness in oilfield production operations, *International Journal of Scientific and Technology Research,* **1(4)**, 19-23.

2. Mobin, M., Khan, M. A. and Parveen, M. (2011) Inhibition of mild steel corrosion in acidic medium using starch and surfactant additives, *Journal of Application Polymer Science,* **121**, 1558-1565.

3. McCafferty, E. (1979) Thermodynamic aspects of the crevice corrosion of iron in chromate/chloride solutions, *Journal of Electro-chemistry Society*, **126(3)**, 385-390.

4. Oribute-Okorosaye, K., Jack, I. R., Ochei, M. and Akaranta, O. (2007) Synergistic effect of potassium iodide on corrosion inhibition of mild steel in HCl medium by extracts of Nypa fructican's Wurmb, *Journal of Applied Sciences and Environmental management,* **11 (2)**, 27-31.

5. Sakawi, Z., Ali, M. H. M., Rostam, K. and Nor, A. R. M. (2010) Impak pengurusan tapak pelupusan ke atas kualiti air sungai di Malaysia: Iktibar dari pengalaman tapak pelupusan Pajam dan Sungai Pajam, Negeri Sembilan, *Malaysian Journal of Society Space,* **6(1)**, 50-59.

6. Raja, P. B. and Sethuraman, M. G. (2008) Natural products as corrosion inhibitor for metals in corrosive media — A review, *Materials Letters,* **62**, 113-116.

7. Omar, I.H., Zucchi, F. and Trabanelli, G. (1986) Schiff bases as corrosion inhibitors of copper and its alloys in acidic media, *Sufrace Coatings and Technology,* **29(2)**, 141-151.

8. Yaakob, N. (2007) Development of palm oil based anticorrosion material for underwater protection, Master Dissertation, University Technology MARA, Malaysia.

9. El-Etre, A. Y. (2007) Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves, *Journal of Colloid and Interface Science*, **314(2)**, 578-583.

10. Obi-Egbedi, N. O. and Obot, J. B. (2012) Adsorption behavior and corrosion inhibitive potential of xanthenes on mild steel/sulphuric acid interface, *Arabian Journal of Chemistry,* **5**, 121-133.

11. Abiola, O. K. and Oforka, N. C. (2003) Inhibition of the corrosion of mild steel in hydrochloric acid by (4-amino-2-methyl-5-pyrimidinymethylthio) acetic acid and its precursor, *The Journal of Corrosion Science and Engineering,* **3(12)**, 1-10.

12. Satar, M. Z. M., Noor, M. F. M., Samsudin, M. W. and Othman, M. R. (2012) Corrosion Inhibition of aluminum by using nipah (*Nypa-fructicans*) extract solutions in hydrochloric acid (HCI) medic, *International Journal of Electrochemica l Science*, **7**, 1958-1967.

13. Eqbal M. A. D., Sani, H. A., Abdullah, A. and Kasim, Z. M. (2011) Fatty acids composition of four different vegetable oils (red palm olein, palm olein, corn oil and coconut oil) by gas chromatography, *IPCBEE,* **14**, 31-34.

14. Abdulkarim, S. M., Myat, M. W. and Ghazali, H. M. (2010) Sensory and physicochemical qualities of palm olein and sesame seed oil blends during frying of banana chips, *Journal of Agricultural Science,* **2(4)**, 18-29.