Surface Morphology Studies of Low Carbon Steel Treated in Aqueous Lignin

(Kajian Morfologi Permukaan Terhadap Keluli Berkarbon
Rendah Terawat dalam Lignin Berakueus)

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ABSTRACT

The effect of corrosion inhibition of low carbon steel in water based medium containing lignin was investigated via weight loss method. The evolution of surface morphology has been carried out for 7 to 42 days via optical microscopy (OM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron microscopy (XPS). Immersion of metal specimen without lignin shows that significant increase in the surface roughness. The longer the immersion time, the more the oxide crust formed. The surface degradation of metal specimen was well protected by immersion in lignin solution. A protective layer containing of lignin was formed on the surface of metal specimens after 7 and 21 days immersion. The corrosion inhibition gives about 13 and 53% inhibition for both 7 and 21 days immersion, respectively. The protective layers were spalling and separated from the metal surface after 42 days immersion in lignin solution possibly due to the increase in corrosion attack after long time immersion according to the increase in dissolved oxygen and may also due to the thermal mismatch between oxide and substrate. The adsorption of protective layer containing lignin was temporary adsorbed on the surface.

Keywords: Adsorption; corrosion; low carbon steel; weight loss method

ABSTRAK

Kesan perencatan kakisan keluli berkarbon rendah dalam medium air yang mengandungi lignin telah dikaji melalui kaedah penurunan berat. Evolusi morfologi permukaan telah dijalankan selama 7 hingga 42 hari melalui mikroskop optik (OM), mikroskopi elektron imbasan (SEM), spektroskopi penyerakan tenaga X-ray (EDX) dan fotoelektron mikroskopi x-ray (XPS). Penyerapan spesimen logam tanpa lignin menunjukkan bahawa peningkatan yang ketara pada kekasaran permukaan. Semakin lama masa rendaman, semakin banyak kerak oksida terbentuk. Degradasi permukaan spesimen logam dapat dikawal dengan merendamkan spesimen dalam larutan lignin. Lapisan pelindung yang mengandungi lignin telah terbentuk pada permukaan spesimen logam selepas rendaman selama 7 dan 21 hari. Perencatan kakisan memberikan perencatan kira-kira 13 dan 53% untuk 7 dan 21 hari rendaman. Lapisan pelindung mengalami pengelupasan dan terpisah dari permukaan logam selepas 42 hari rendaman dalam larutan lignin mungkin disebabkan oleh peningkatan serangan kakisan selepas masa rendaman yang lama menyebabkan peningkatan oksigen terlarut dan mungkin juga disebabkan oleh ketidakpadanan haba antara oksida dan substrat. Penjerapan lapisan pelindung yang mengandungi lignin merupakan perjerapan sementara pada permukaan logam.

Kata kunci: Kaedah kehilangan berat; kakisan; keluli berkarbon rendah; penjerapan

INTRODUCTION

Corrosion is the primary means by which metals deteriorate. Most metals corrode on contact with water (and moisture in the air), acids, bases, salts, oils, aggressive metal polishes and other solid and liquid chemicals. Corrosion control is important in extending the life of equipment. This natural phenomenon needs to be controlled in order to avoid waste of cost during the application of metallic materials. Basically, the main idea of this research was to develop the potential of local biomass residue as novel materials used in corrosion protection. The application of green and organic corrosion inhibitors is one of the most practical methods for protection against corrosion. An organic corrosion inhibitor containing lignin from various plant sources is reported to be able to reduce metal corrosion. In Southeast Asia, lignin can be found in rice straw of paddy plant waste and empty fruit bunch of palm oil plant. Previous studies have shown that lignin can give up to 80% corrosion inhibition via fast testing method (electrochemical measurement) in acidic and near neutral medium (Akbarzadeh et al. 2011; Altwaiq et al. 2011; Dong et al. 2011; Ren et al. 2008; Vagin et al. 2006). However, the sustainability of treated metal by lignin as corrosion inhibitors in water based medium are rarely investigated. The objective of this work was to study the surface morphology effect on low carbon steel in water based medium with and without immersion in lignin as green corrosion inhibitor.

METHODS

Low carbon steel coupons with composition Fe 99.3%, C 0.12%, Mn 0.5%, P 0.04%, S 0.045% were used in this experiment. Prior to analysis, all coupons were polished with 800 to 1200 grades of abrasive papers, washed thoroughly with acetone and distilled water and finally dried at room temperature (26℃). The polished and pre-weighed coupons were immersed for a period of 7, 14, 21, 28, 35 and 42 days in water with and without lignin 1500 ppm. Then the specimens were taken out, washed, dried and weighed according to ASTM G1-03. 2004 (ASTM G1-03 2004). All samples were analyzed via optical microscopy (OM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) SEM-EDX and X-ray photoelectron microscopy, XPS.

RESULTS AND DISCUSSION

CORROSION RATE AND INHIBITION STUDIES
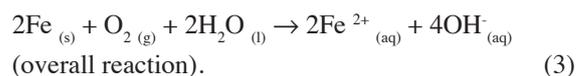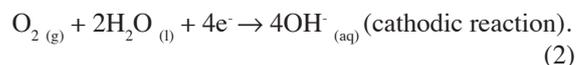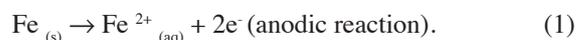
Figure 1 shows the results of corrosion rate and inhibition efficiency (%IE) of low carbon steel after immersion with and without lignin through weight lost measurement. From the graph, immersion of metal specimens without lignin from 7 to 42 days shows high in corrosion rate values compared with immersion in lignin. The value of %IE increased from 13 to 53% at 7 to 21 days immersion. However, after 21 to 42 days immersion, the corrosion rate of metal increased, followed by the fluctuated value of corrosion rate even treated in lignin solution. The concentration of dissolved oxygen in the electrolyte aqueous solution may be one of the factors influencing the rate of corrosion for the specimen. At ordinary temperatures (26°C), the absence of dissolved oxygen will greatly slow the corrosion of ferrous metals (Sastri et al. 2007). In fact, oxygen is a direct participant in the corrosion reaction, acting as a cathode-accepting electron. In this study, since the immersion time has been extended, the level of oxygen concentration may also be increased as the rate of the electron transport increases. As a result, the rate of corrosion for the specimen increased with any increased of dissolved oxygen. Thus, the inhibition

efficiency becomes low. Nevertheless, lignins still capable to inhibit the corrosion process until 42 days.

SURFACE ANALYSIS STUDIES

Figure 2 shows the photograph of carbon steel immersed in lignin and without lignin solution after 7, 21 and 42 days. Immersion of the metal specimen without lignin after 7, 21 and 42 days shows the metal specimen surfaces (typical shiny appearance) turned to black color, suggested as magnetite, Fe_3O_4 (Figure 2(a), 2(b) and 2(c)) (Sastri et al. 2007). More corrosion products with brown color suggested as hematite, Fe_2O_3 (McCafferty 2009) observed on the specimen surface since the immersion in solution without lignin has been extended to 42 days as can be seen in Figure 2(c). Immersion in lignin solution exhibits that the specimens's surface covered with the lignin layer (Figure 2(d), 2(e) and 2(f)). The lignin film was clearly observed after immersion at 7 and 21 days. However, after immersion at 42 days, lignin film was possibly incapable to strongly adsorb on the metal surface. The thin lignin layer could be impermanent or no longer attached on the specimen surface over the extended time immersion. The continuous corrosion attack caused by increase in dissolved oxygen may be the factor of the detached protective lignin layer.

The mechanism of corrosion is as follows (McCafferty 2009). The carbon steel surface consists of a region, which acts as an anode. Oxidation occurs at the anodic site. Since there is oxygen in the atmosphere, reduction occurs at another region of the carbon steel surface.

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \text{ (anodic reaction).} \qquad (1)$$

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} \text{ (cathodic reaction).} \qquad (2)$$

$$2Fe_{(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + 4OH^-_{(aq)}$$
(overall reaction). $\qquad (3)$

Continous reaction occurs with the formation and precipitation of iron hydroxide, $Fe(OH)_2$ on carbon steel surface.
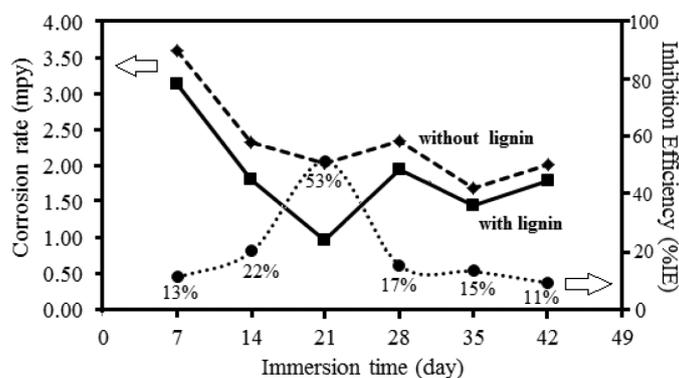

FIGURE 1. Corrosion rate of carbon steel after immersion with and without lignin and the inhibition efficiency
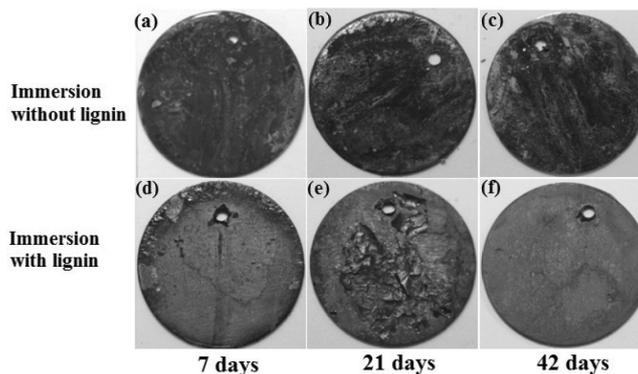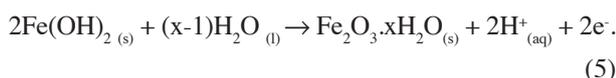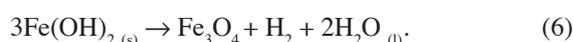
FIGURE 2. Macroscopic images of carbon steel after 7, 21 and 42
days immersion in solution with and without lignin

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2\ (s)}. \tag{4}$$

Since the iron hydroxide $Fe(OH)_2$, was not thermodinamically stable, it is converted to more thermodynamically stable compounds, hydrated iron oxide, $Fe_2O_3.xH_2O$ (brown rust/hematite).

$$2Fe(OH)_{2\ (s)} + (x-1)H_2O_{(l)} \rightarrow Fe_2O_3.xH_2O_{(s)} + 2H^+_{(aq)} + 2e^-. \tag{5}$$

Prior to the compound conversion above, iron hydroxide $Fe(OH)_2$ can also be transform into Fe_3O_4 (black magnetite) after being oxidized by the proton from water.

$$3Fe(OH)_{2\ (s)} \rightarrow Fe_3O_4 + H_2 + 2H_2O_{(l)}. \tag{6}$$

Micrograph image of specimen surface has been identified via SEM as shown in Figure 3. Immersion for 7 days without lignin shows a tiny ball-like structure of corrosion products (Figure 3(a)) homogeneously distributed overall of the inspection surface. While immersion for 21 days shows the agglomeration of tiny ball-like structures of the corrosion products (Figure 3(b)) followed by formation of long and sharp coral-like structures (Figure 3(c)) of corrosion products since the immersion time has been extended to 42 days. Immersion of metal specimen without lignin shows that significant increased in the surface roughness. Immersion of specimen in lignin shows a flakes of lignin layer covered the metal surface (Figure 3(d)) and was spalling after 21 (Figure 3(e)) and 42 (Figure 3(f)) days immersion.

Table 1 shows the elemental compositions of carbon steel specimens immersed in solution with and without lignin determined using EDX. These compositions have been examined via specific region as marked in Figure 4. Specimens without lignin in Region 1a (Figure 4(a), 4(b), 4(c)) shows high percentage of oxygen (O) and iron (Fe) elements compared to carbon (C) due to the corrosion products properties. Investigation of specimen surface immersed in lignin solution has been observed on two regions. Region 2a (Figure 4(d), 4(e), 4(f)) shows high in Fe contents in all immersion time studied, represented
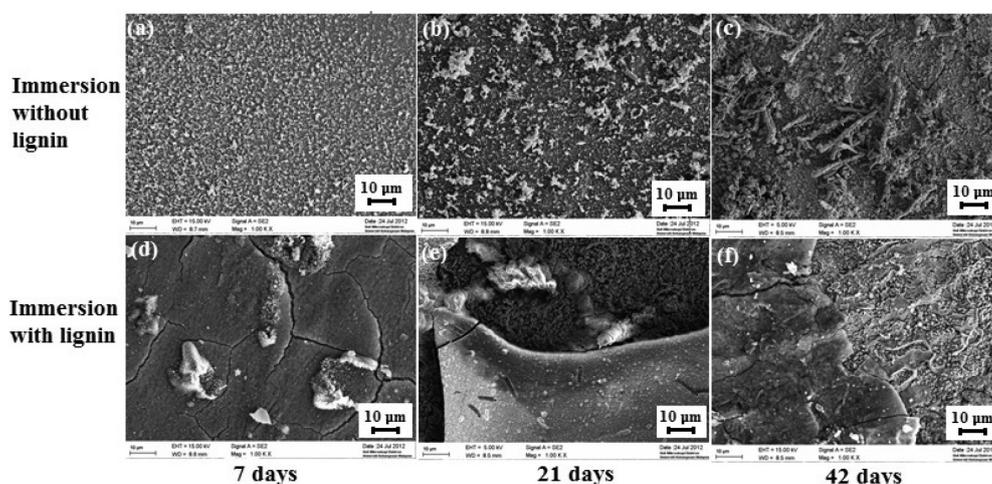

FIGURE 3. SEM micrographs of carbon steel surfaces after 7, 21 and 42 days immersion
in solution with and without lignin

TABLE 1. Elemental composition (weight %) of carbon steel specimen immersed in solution with and without lignin determined using EDX

Immersion time (day)	Without lignin (Region 1)	With lignin	
		(Region 2a)	(Region 2b)
7 days	C=2.14, O=21.64, Fe=76.22	C=2.40, O= 0, Fe=97.60	C= 7.69, O= 31.84, Fe= 60.64
21 days	C= 2.34, O= 10.51, Fe=87.15	C=5.53, O= 4.77, Fe=89.70	C=12.81, O= 36.38, Fe= 50.81
42 days	C=1.04, O=22.52, Fe=76.44	C=7.58, O=4.80, Fe=87.62	C= 5.41, O= 19.42, Fe= 75.17

the specimen surface that uncovered by lignin layer. Region 2b (Figure 4(d), 4(e), 4(f)) shows decreased in Fe contents, otherwise C contents were more pronounced. This element (C) could be described as carbon originated from the lignin which has been adsorbed/ deposited on the specimen surface. The lignin layer provides inhibition to corrosion attack. However, a different value in elemental composition was observed after 42 days immersion in lignin, whereby the C content was reduced. This is resulted from the impermanent adherent of lignin layer on the specimen surfaces. The extended immersion time may cause the corrosion products more occupied on the specimen surface compared to a thick layer of lignin film. The longer the exposed time to corrosive medium (water and dissolved oxygen), the higher the corrosion attacks even in the presence of lignin.

The analysis of chemical species presented on the specimen surface has been performed via XPS. The obtained values of binding energy (BE) and relative percentage of the peak component are summarized in Table 2. From the analysis, a typical corrosion products were consist of mixture of iron oxide and hydroxide; iron (III) oxide (Fe_2O_3)/hematite, iron (II,III) oxide (Fe_3O_4)/magnetite and iron hydroxide (FeOOH)/lepidocrocite.

In general, for organic lignin compounds, the chemical shift of carbon C 1s is usually deconvoluted into six components: C–C (~284.6 eV), C–H (~285.2 eV), C–O (~286.0 eV), C=O (~287.4 eV) and O–C=O (~288.9 eV). The O 1s were fitted with three components, C–O (~531.4 eV), –OH/C=O (~532 eV) and O^{-2} (~530.2 eV) (Merdy et al. 2002). Figure 5 shows the XPS deconvoluted profiles of O 1s, C 1s and Fe 2p of carbon steel after immersion in lignin solution. Overall, the spectrum shows the binding energy seems to shift backward with the extended immersion time. The deconvoluted C 1s spectrum shows high intensity peak at BE=286.0 eV (74.29%) assigned as a lot of C-O components originated from lignin occupied/ adsorbed on metal surface for 7 days immersion. The peak has the largest contribution and also attributed to the C-C, C=C and C-H aromatic bonds of lignin. It is expected that the longer the immersion time, the C components represented as lignin layer was diminished as can be observed through reduction in intensity of peak in C 1s spectrum for 21 and 35 days immersion. This result supports the observation via macroscopic image in Figure 2(d), 2(e), 2(f) and SEM-EDX results of elemental composition. The O 1s spectrum shows peak at range of BE=527.9 to 530.9 eV was attributed to O^{2-} of oxygen bonded to Fe^{3+} in the FeO and/or Fe_2O_3 oxide. A peak at approximately BE~531.0 eV was ascribed to OH^- assigned as oxygen in hydrous iron oxides such as FeOOH and/ or $Fe(OH)_3$. Oxygen of adsorbed water was assigned by peaks at range of BE=533.1 to 534.7 eV. The oxygen of C-O (typical BE~531.4 eV) and OH^- (typical BE~532.0
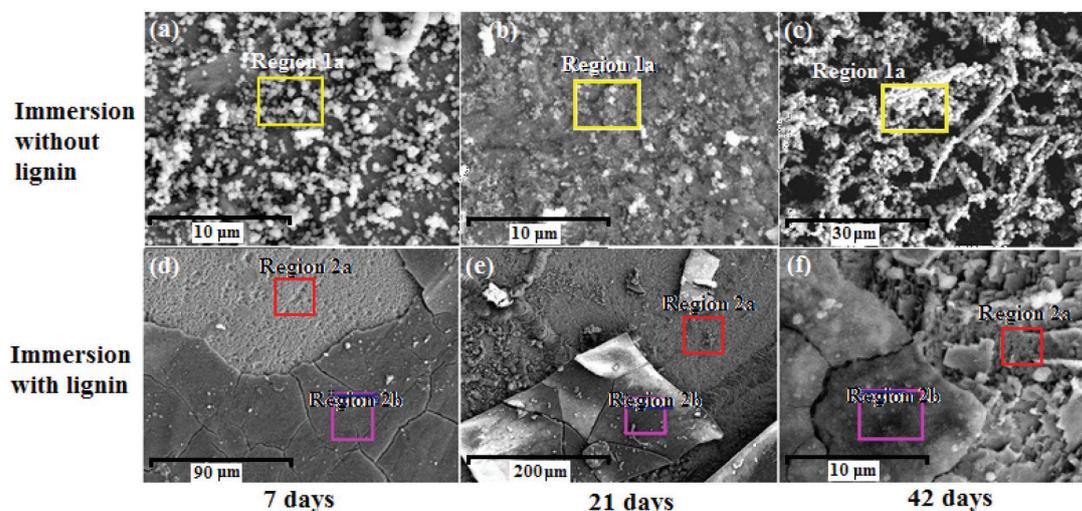

FIGURE 4. SEM-EDX micrographs of carbon steel surfaces after 7, 21 and 42 days immersion in solution with and without lignin

TABLE 2. Binding energy, BE (eV) and assignment of carbon steel specimen
immersed in lignin determined using XPS

| Element	Immersion in lignin		
	7 days	21 days	35 days
C 1s	284.5 (10.2%)	284.8 (74.22%)	282.7 (45.42%)
	286.0 (74.29%)	286.2 (16.63%)	284.5 (34.46%)
	288.0 (8.35%)	288.3 (9.15%)	287.2 (12.84%)
	289.9 (7.16)		290.6 (7.27%)
O 1s	531.7 (26.09%)	530.1 (47.06%)	527.9 (41.11%)
	533.2 (62.94%)	531.5 (41.22%)	529.3 (48.23%)
	534.7 (10.97%)	533.1 (11.72%)	530.9 (10.66%)
Fe 2p	710.9 (20.09%)	710.8 (37.77%)	709.8 (35.02%)
	711.8 (37.59%)	712.9 (19.18%)	713.7 (10.94%)
	724.6 (14.59%)	715.3 (8.46%)	717.6 (14.94%)
	725.9 (27.74%)	724.3 (17.81%)	723.4 (21.78%)
		726.4 (14.24%)	727.3 (9.12%)
		729.3 (2.54%)	731.2 (8.20%)

(a)

(b)

(c)
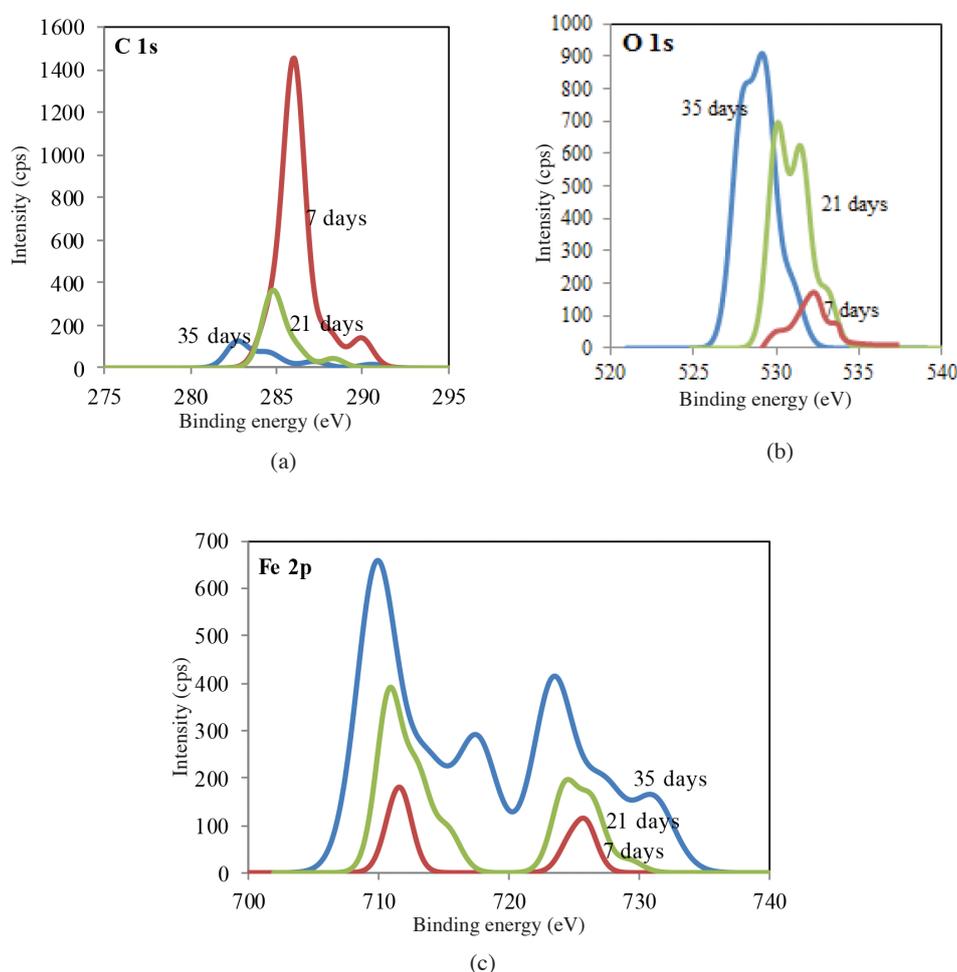
FIGURE 5. The XPS deconvoluted profiles of (a) C 1s (b) O 1s and (c) Fe 2p of carbon
steel after immersion in lignin solution

eV) also may be originated from the lignin compounds itself. Both functional group may be coordinated to the carbon steel surface and caused the peak shift towards higher binding energy (BE=533.1, 533.2 and 534.7 eV).

The Fe 2p spectrum for metal specimen immersed in lignin shows the first peak for 35 days immersion located at BE=709.8 eV was assigned to metallic iron (Fe^0). The second and third peak at BE=710.8 eV (21 days) and

710.9 (7 days), respectively, assigned to Fe^{3+} that was attributed to the ferric compounds such as Fe_2O_3 (i.e. Fe^{3+} oxide) and/or Fe_3O_4 (i.e. Fe^{2+}/Fe^{3+} mixed oxide) and FeOOH (i.e. oxyhydroxide) (Bentiss et al. 2012). The longer the immersion time, the more the peak of ferric compounds appeared and the higher the intensity of ferric components. The binding energy of each ferric compounds on the specimen immersed in lignin increased as immersion time decreased.

CONCLUSION

From this study, it can be concluded that corrosion rate of carbon steel can be reduced with treatment in lignin solution. Lignin was capable to inhibit corrosion of carbon steel in water based medium until 42 days immersion. Surface analysis via OM, SEM and SEM-EDX revealed the appearance of lignin layer were mostly covered on the metal surface after 7 days immersion and showed impermanent adherent of protective layer after 21 and 42 days immersion. XPS analysis claimed the higher the immersion time, the lower the intensity peak of C 1s, O 1s and Fe 2p components represented the greater the corrosion products left on the metal surface. The coordination and interaction between metal surface and lignin compounds may occur as deduced by the shift of binding energy towards high values as discussed above.

ACKNOWLEDGMENTS

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