Depolymerized Oil Palm Frond (OPF) Lignin Products as Corrosion Inhibitors for Mild Steel in 1 M HCl

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The inhibitory effects of depolymerized alkaline soda (OSL), kraft (OKL) and organosolv (OOL) lignin products via nitrobenzene oxidation method on mild steel corrosion in 1.0 M HCl medium were investigated by using weight loss measurement, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods. The corrosion inhibition efficiency obtained from all methods was found to increase with increased concentrations for all depolymerized lignin products. Polarization measurements indicated that OSL, OKL, and OOL acted as mixed type inhibitors. Ferric reducing power activity of OSL, OKL, and OOL that has been determined via reducing power assay showed that all three inhibitors have the ability to act as antioxidants. The adsorption behavior of OSL, OKL, and OOL products was also studied; the experimental data have been found to well fit the Langmuir adsorption isotherm and the ΔG°_{ads} values proved that physisorption dominated the adsorption process. High-performance liquid chromatography (HPLC) analysis was carried out to quantify the fractions of depolymerized lignin and seven phenolic constituents (p-hydroxybenzoic acid, vanillic acid, syringic acid, *p*-hydroxybenzaldehyde, vanillin, syringaldehyde, and *p*-hydroxyacetophenone) were found to be present in OSL, OKL, and OOL; out of which, three (syringaldehyde, vanillin, and phydroxybenzaldehyde) were identified as the main compounds responsible for corrosion inhibition of mild steel in 1 M HCl medium. The analysis revealed that only phenolic aldehydes (S, V and 4-HB) gave significant contributions to the corrosion inhibition for mild steel in 1 M HCl that do not depend on the total initial concentration of S, V and 4-HB in the depolymerized lignin products. The results from the HPLC analysis corroborates well with the electrochemical and weight-loss measurements results. The surface morphology of mild steel was monitored by scanning electron microscopy (SEM). It was observed that the roughness of the surface was reduced with the addition of an inhibitor as compared to the one without an inhibitor indicating reduced corrosion rate of mild steel that is supported by the X-ray diffraction (XRD) analysis.

Keywords: Lignin, corrosion inhibitor, electrochemical, mild steel corrosion, HPLC

Acids are widely applied in many industries such as synthesis process in chemical and petrochemical industry, for chemical cleaning before galvanizing, phosphatizing, passivation, or other coating uses, boilers, heat exchangers, petroleum equipment and also for removal of undesirable material and rust in the metal finishing industries [1-5]. Among acid solutions, hydrochloric acid (HCl) is one of the most widely used. It is the most difficult acid to handle whereby extra care is required, even in relatively lower concentration. This acid is also very corrosive to most metals and alloys [6]. Corrosion control offers the cost-effective ways to reduce premature deterioration of materials. There are three common methods to control corrosion. They include protective coatings and linings, cathodic/anodic protection and corrosion inhibitors. Among these methods, utilization of corrosion inhibitors is one of the most convenient methods for erosion protection and is very useful in industries. This method is preferred because it is cheap and very practical. In recent years, due to the growing interest and attention to environment protection and the risk of using chemicals on the ecological balance, the corrosion inhibitors approach has gradually changed [7]. Nontoxic and natural inhibitors have become alternatives to replace toxic inhibitors because they are environmental friendly in nature, readily available and are renewable sources [8,9]. Non-toxic compound and natural products of plant extraction, e.g. extract of some seeds [10] and leaves [11] are categorized as environmental friendly or ecological acceptable materials.

Oil palm fronds (OPF) are deposited on oil palm plantations form about 60% of solid biomass volume [12]. In order to ensure soil nutrient conservation, during pruning and harvesting, these fronds are usually left in the plantation [13-15]. Furthermore, several studies have been reported on the potential applications of OPF; for examples, as a source of fiber for animal feeds [15] and nutraceuticals [16]. It was also found that the fermentation of OPF juice could produce various value-added products, such as polyhydroxyalkanoates (PHA), bioethanol, biobutanol, lactic acid, and succinic acid [12]. It has also been employed in biofuel regeneration [17,18], as absorbent for heavy metal ions in wastewater [19], renewable sugar [15,20], composite board [21], and raw materials to produce paper via chemical pulping processes [22-24]. The pulping process produces black liquor that generates lignin as by-product through precipitation.

Lignin is labeled as waste material with limited utilization or traditionally underutilized. However, Stewart [25] has made a survey and desk study to review changes and patterns in the utilization of lignin. It is shown that over the last 10–15 years, there were many researches on commercialization of lignin-based products and processes. Existing applications of lignin and numerous potential utilizations were investigated and discussed by many researchers [25-27]. They also addressed the depolymerization of lignin molecules into valuable aromatic monomers as paths to promote the lignin utilization. Nitrobenzene was one of the initial chemical oxidants used to depolymerize lignin. Besides, nitrobenzene oxidation method is commonly used to determine and estimate the S/G ratio of lignin, depending on the source of lignin [28-34]. In the alkaline nitrobenzene oxidation, lignin is cleaved to form aromatic carbonyl compounds, i.e. syringaldehyde and vanillin as the main products. The yield of the carbonyl compounds from nitrobenzene oxidation method is approximately only 50% of the lignin due to the lack of reactivity of nitrobenzene oxidation against condensed structures [35]. This oxidation method is chosen in order to study the potential of depolymerized lignin products as corrosion inhibitors.

The present work aims at developing eco-friendly corrosion inhibitor from the use of agricultural plants parts, usually discarded as waste (lignocellulosic biomass from oil palm frond). It is reported that the alkaline lignin extracted from oil palm frond (OPF) and oil palm empty fruit bunches (OPEFB) can act as good corrosion inhibitors of mild steel in acidic and sodium chloride mediums, respectively [36-38]. In the present work, the use of depolymerized alkaline and organosolv lignin products have been evaluated as corrosion inhibitors for mild steel in HCl medium. The corrosion behavior was evaluated by using weight loss measurement, electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization. The morphology of inhibited mild steel surfaces was analyzed via scanning electron microscope spectroscopy (SEM) and X-ray diffraction (XRD) was used to analyze corrosion products formed on the mild steel surface. Meanwhile high-performance liquid chromatography (HPLC) was used to quantify the amount of monomers consumed in the corrosion inhibition process and was correlated to the inhibition efficiency.

2. EXPERIMENTAL

2.1 Raw material and pulping condition

The OPF used for kraft, soda and organosoly pulping were obtained from the oil palm plantation at Mersing, Johor, Malaysia, in early 2012. The typical chemical composition of OPF are cellulose, 31.0%, hemicelluloses, 17.1%, kalson lignin, 22.9%, wax, 2.0%, ash, 2.8%, and others; 24.2%, as reported by [39]. The pulping processes were carried out in a 4-L rotary digester. The pulping conditions for kraft and soda followed the method outlined by [23] with slight modifications [40]. For kraft pulping, 20% of active alkali and 30% of sulfidity with water to fiber ratio of 8 were used. The time of maximum cooking temperature (170 °C) was set for 3 h. For soda pulping, 30% of active alkali alone was applied with the same condition as previously described. The pressure of both kraft and soda pulping was around 12–15 bar. The black liquor was collected by filtration of the pulp. The concentrated black liquor was then acidified with 20% (v/v) sulfuric acid to pH 2 to precipitate the soda and kraft lignins [41]. Then, the precipitated lignins were filtered and washed with pH 2 water. Both lignins were oven dried at 50 °C for 48 h. Lignin was purified by extracting lignin with n-pentane using the soxhlet apparatus for 6 h to remove lipophilic non-lignin matters, such as wax and lipids. The lignin was then filtered and washed with pH 2 water to remove excess n-pentane and non-lignin phenolic compounds which may remain after the extraction process. Purified kraft and soda lignins were then oven dried for another 48 h.

Meanwhile, organosolv pulping conditions followed the method outlined by the previous study [40] with slight modifications. The pulping process was performed by mixing the OPF with the solvent (60%, w/w aqueous ethanol) in a ratio of 10 L kg⁻¹ dry biomass with 0.5% (w/w) sulfuric acid as a catalyst at 190 °C for 60 min. The pressure of organosolv was then maintained throughout the experiment at 25 bar. Subsequently, the digester was cooled down to below 40 °C after the pulping

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process. The organosolv pulp was then filtered using Whatman type 1 paper filters and the solid fraction was washed with cooking liquor. After that, the filtrate or organosolv liquor was diluted with water: solution 3:1 (v/v) to precipitate the ethanol organosolv lignin. The precipitate was then collected by centrifugation at 3500 rpm for 10 min. The resulting ethanol organosolv lignin was oven dried at 50 °C for 48 h.

2.2 Depolymerization of lignin by nitrobenzene oxidation method

The nitrobenzene oxidation method was slightly modified from the previous study [42]. The process was carried out by dissolving 50 mg of each dry soda, kraft and organosolv lignin from OPF with 7 mL of 2 M NaOH and then 0.42 mL of nitrobenzene was added into the mixture. The mixture was then put in a 15 mL steel autoclave, sealed and heated to 170 °C for 3 hrs in a preheated oil bath. After the process, the autoclave was cooled to ambient temperature. The mixture was then transferred to a liquid-liquid extractor for the extraction process with chloroform (5-15 mL) to remove any nitrobenzene reduction products and excess of nitrobenzene that may remain after the oxidation process. After that, the oxidation mixture was acidified with concentrated HCl to pH 3-4 and further extracted with chloroform (5-10 mL). Chloroform used in the second extraction procedure was removed by using a rotary evaporator at 40 °C under reduced pressure to obtain the oxidation mixture. The mixture was then oven dried at 40 °C and the process was repeated several times. Then the oxidation products were dissolved in methanol and made up to 10 mL. This mixture was used as a stock solution for further analysis.

2.3 Reducing power assay

The reducing power was determined according to the method by [43] with slight modifications. Various concentrations of OSL, OKL, and OOL (3.0 mL) were mixed with 2.5 mL of 0.2 M sodium phosphate buffer (pH 6.6) and 2.5 mL of 1% potassium ferricyanide. The mixture was incubated at 50 °C for 20 min. After 2.5 mL of 10% trichloroacetic acid (w/v) was added, the mixture was centrifuged at 6000 rpm for 5 min. The upper layer (5 mL) was mixed with 5 mL of deionized water and 1 mL of 0.1% of ferric chloride, and the absorbance was spectrophotometrically measured at 700 nm. Syringaldehyde, vanillin, and 4-hydroxybenzaldehyde at various concentrations were used as standards.

2.4 Specimen preparation for corrosion study

The mild steel coupons used had the following chemical composition (in weight percent) of Fe 99.54, C 0.06, Mn 0.29, Al 0.04 P 0.01 and S 0.06. All coupons surfaces were polished with 400 to 1000 grades of abrasive paper washed with ethanol and distilled water and finally dried with soft paper. Rectangular coupons of a total surface area of 6.4 cm² were used for weight loss measurements. For electrochemical measurements, mild steel coupons with the dimension of 3 cm x 3 cm x 0.05 cm

were used with an exposed area of 3.142 cm^2 . 1 M HCl solution was used as test solution in both methods. Depolymerized products were first dissolved in 10% (v/v) of methanol to increase solubility. The dissolved depolymerized products were next diluted with 1 M HCl (AR grade). Different concentrations of inhibitor were obtained by diluting the stock solution to obtain 50, 100, 200, 300 and 400 mg mL⁻¹ solutions.

2.4.1 Weight loss method

For the weight loss measurements, experiments were conducted in the test solution with the presence and absence of depolymerized products at ambient temperature (29 ± 1 °C). In each experiment, the cleaned mild steel sample was weighed and immersed in 30 mL acid solutions. After 24 h immersion, the sample was then taken out of the test solution, rinsed with distilled water, dried and weighed. To ensure high accuracy in measurements, three sets of the samples were used at each inhibitor concentration. The average weight loss value was used to calculate the corrosion inhibition efficiencies at different concentrations of OSL, OKL, and OOL (η_{WL}) were calculated by using the following equations:

$$\eta_{WL}(\%) = \frac{W_o - W_i}{W_o} \times 100 \tag{1}$$

$$\theta = \frac{W_o - W_i}{W_o} \tag{2}$$

where W_o and W_i indicate the weight loss of mild steel coupon in the absence and presence of inhibitor respectively, and θ is surface coverage value. Additionally, corrosion rates (C_r) from weight loss measurements at various concentrations of inhibitor were determined from the following equation:

$$C_r \left(mg \ cm^{-2} \ h^{-1} \right) = \frac{\Delta W}{At}$$
(3)

where ΔW is the weight loss of the sample in mg, A is the area of the exposure in cm², and t is immersion time in hours.

2.4.2 Potentiodynamic polarization measurement

Potentiodynamic polarization measurements of electrochemical tests were carried out at ambient temperature. A conventional three-electrode system was used in the experiment, where a platinum electrode was used as a counter electrode, a saturated calomel electrode (SCE) was used as a reference electrode and mild steel coupons as a working electrode, respectively. All three electrodes were immersed in 50 mL of test solution. The analysis was then carried out using Potentiostat/Galvanostat/ZRA Model Gamry Reference 600 and the data were analyzed using the

Gamry Instrument Framework version 5.67 software. Prior to each measurement, the electrode was kept in the test solution at the natural potential for 30 minutes, which provided sufficient time for open circuit potential, E_{ocp} , to attain stabilization of the steady-state potential. The polarization potential was recorded from a cathodic potential of -300 mV to an anodic potential of +300 mV with respect to the corrosion potential, E_{corr} , at a scan rate of 1 mVs⁻¹. Corrosion current density values, I_{corr} , were obtained by extrapolating the linear sections from the anodic and cathodic curves to corrosion potential, E_{corr} , and the inhibition efficiency (η_P) at different inhibitor concentrations was calculated according to the following equation:

$$\eta_P(\%) = \frac{I_{corr_{(o)}} - I_{corr_{(i)}}}{I_{corr_{(o)}}} \times 100$$
(4)

where $I_{corr(o)}$ and $I_{corr(i)}$ belong to the corrosion current density without and with the addition of inhibitor. Meanwhile, the linear polarization resistance (LPR) method was used to calculate polarization resistance (R_p). Then, polarization resistance values were used to calculate the inhibition efficiency (η_{PR}) in the presence and absence of inhibitors by using the following formula:

$$\eta_{PR}(\%) = \frac{R_{p_{(i)}} - R_{p_{(o)}}}{R_{p_{(i)}}} \times 100$$
(5)

where $R_{P(i)}$ and $R_{P(o)}$ denote linear polarization resistance in the presence and absence of inhibitors, respectively.

2.4.3 Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range from 100,000 to 0.1 Hz with AC amplitude of 10 mV rms at open circuit potential and scan rate of 10 points decade⁻¹. The Nyquist and Bode plots representation of the impedance data were analyzed using the Gamry Instrument Framework version 5.67 software. Charge transfer resistance (R_{ct}) was obtained by fitting the Nyquist semicircle plots to equivalent circuit as shown in Fig 5(d). Inhibition efficiency (η_E) was calculated at each inhibitor concentration according to the following equation:

$$\eta_E(\%) = \frac{R_{ct_{(i)}} - R_{ct_{(o)}}}{R_{ct_{(i)}}} \times 100$$
(6)

where $R_{ct(o)}$ and $R_{ct(i)}$ indicate charge transfer resistance in the absence and presence of various concentrations of inhibitor, respectively.

2.5 High-performance liquid chromatography (HPLC)

The HPLC analysis of OSL, OKL, and OOL products was performed by using HPLC (SCL-10A VP Shimadzu) with the system controller of SPD-10A VP Shimadzu UV/Vis and was equipped with BDS Hypersil Gold C₁₈ column (4.6 mm x 250 mm, with particle size 5 μ m). The detection wavelength was set at 280 nm. Analyses were run at room temperature, 29 °C, with a flow rate of 1.0 mL min⁻¹. Volume injection was 20 μ L. All data were analyzed by using the data processing software Shimadzu CLASS-VP version 6.12 SP2. All samples were filtered through nylon membrane filters with a pore size of 0.45 μ m. The separation was performed using isocratic eluent. The mobile phase used was water; methanol: acetonitrile: acetic acid (79:13:07:1 v/v). The phenolic aldehydes, ketone, and acids in OSL, OKL, and OOL were identified by comparison of their experimental retention times with the retention times of pure compounds. The total consumption of OSL, OKL, and OOL during the corrosion process was quantified by using standard calibration curves of pure compounds.

2.6 Surface analysis

The surface morphology of the mild steel specimens was evaluated using scanning electron microscope spectroscopy, SEM analysis (Leo Supra 50VP) at the magnification of 1500x. X-ray diffraction, XRD patterns (PANalytical X'Pert PRO MRD PW3040) was used for the analysis of corrosion products formed on the mild steel surface. For this purpose, the test specimen which exhibited the highest efficiency of corrosion inhibition from the weight loss measurement was examined together with the blank (without the inhibitor).

3. RESULTS AND DISCUSSION

3.1 Ferric reducing power

Reducing power may provide a significant indicator to determine the antioxidant activity of compounds [44], where compounds with the presence of antioxidants (reducing power) act as an electron donor that would result in the reduction of Fe³⁺/ferricyanide complex used in this assay to the ferrous form. It is possible to determine the concentration of Fe^{2+}/Fe^{3+} ion by measuring the formation of Pearl's Prussian blue at 700nm [45]. In this assay, the yellow color of test solution changed to the various dark colors of green and blue depending on the reducing power of each compound [45, 46]. The ferric reducing powers of OSL, OKL, and OOL were determined by comparing with the standard compounds of syringaldehyde, vanillin, and 4-hydroxybenzaldehye. The three standard compounds were chosen to mimic the reduction ability of syringyl (S) guaiacyl (G) and hydroxyl (H) units in The reducing powers of syringaldehyde, depolymerized lignin products. vanillin, 4hydroxybenzaldehyde, OSL, OKL and OOL with the function of their concentrations are shown in Figure 1. The absorbance values of all analytes are presented in Table 1. It is observed that the increased absorbance values with increased concentrations of the OSL, OKL, and OOL at 700 nm as

shown in Figure 1, indicating an increase in reductive ability. The reducing powers of the three standards were found to be lower than all the depolymerized lignin products, except for OOL products, which were found to be slightly lower than syringaldehyde. As shown in Table 1 in the concentration range of 20 to 100 mg L^{-1} , the reducing powers of OSL, OKL, and OOL were 0.069–0.298, 0.118–0.450 and 0.039-0.075, respectively, whereas those of syringaldehyde, vanillin and 4-hydroxybenzaldehyde were 0.061–0.144, 0.043-0.050 and 0.035-0.036, respectively. It was found that the reducing powers of the depolymerized lignin products increased with the increase of their concentrations and suggested that the reducing power increase might be due to the increase of phenolic content of the depolymerized lignin products [46]. This also signified the ability of depolymerized lignin products to convert free radicals into more stable nonreactive species and to terminate radical chain reactions [46]. This property could be advantageous for the use of depolymerized lignin products as a source of antioxidant compounds to delay or inhibit any oxidative reaction. Thus, it could be proposed that the addition of antioxidants may prevent adverse effects caused by oxidation, such as corrosion of metals [47].



Figure 1. Reducing activity of syringaldehyde, vanillin, 4-hydroxybenzaldehyde, OSL, OKL and OOL obtained at 700 nm.

Table 1. Ferric reducing power results (optical density) of OSL, OKL, and OOL at 700 nm.

Concentration (mg L ⁻¹)	OSL	OKL	OOL
20	0.069±0.003	0.118±0.010	0.039 ± 0.001
40	0.143±0.005	0.213±0.005	0.046 ± 0.001
60	0.191±0.007	0.253±0.002	0.057 ± 0.001
80	0.226±0.001	0.366 ± 0.003	0.067 ± 0.001
100	0.298±0.011	0.450 ± 0.021	0.075 ± 0.001
	Syringaldehyde	Vanillin	4-hydroxybenzaldehyde
20	0.061±0.006	0.043±0.001	0.036 ± 0.002
40	0.079±0.003	0.043 ± 0.001	0.035 ± 0.003
60	0.100 ± 0.004	0.048 ± 0.001	0.035 ± 0.001
80	0.108 ± 0.006	0.047 ± 0.001	0.036 ± 0.001
100	0.144 ± 0.004	0.050 ± 0.001	0.036 ± 0.001

3.2 Weight loss method

The inhibition efficiency $\eta_{WL}(\%)$ values and corrosion rate (C_r), obtained from the weight loss method, using equations (1) and (3), at different concentrations of depolymerized lignin products after 24 h of immersion in 1 M HCl at 29 ±1 °C are assembled in Table 2. It is shown that the inhibition efficiency, $\eta_{WI}(\%)$ enhanced with the inhibitor concentration, while, with increased inhibitor concentrations, the corrosion rate (C_r) of mild steel decreased gradually, indicating that the corrosion of mild steel was slowed down by the OSL, OKL, and OOL. As stated in Table 2, the maximum values of $\eta_{WL}(\%)$ for OSL, OKL, and OOL are 97.7, 93.9 and 94.1% respectively, at 400 mg L⁻¹ of inhibitors. The inhibitory effect of OSL, OKL, and OOL as presented in Figure 2, showed that the η_{WL} increased sharply with concentration when the concentrations of OSL, OKL, and OOL were less than 200 mg L^{-1} whereas a gradual increase of η_{WL} can be observed as OSL, OKL, and OOL concentration increased from 200 to 400 mg L⁻¹. It was found that the η_{WL} reached maximum values at 400 mg L⁻¹ for all inhibitors. These results indicated that OSL, OKL, and OOL are good corrosion inhibitors for mild steel in 1 M HCl medium and the corrosion inhibition property of depolymerized lignin products can be attributed to the adsorption of phenolic aldehydes, ketone and phenolic acids in depolymerized lignin products on the mild steel surface which increased the surface coverage area as well as suppressed corrosion reaction rate [48].

Concentration (mg L ⁻¹)	$\eta_{WL}(\%)$	$C_r ({\rm mg}{\rm cm}^{-2}{\rm h}^{-1})$
Blank	-	1.08 ± 0.003
OSL		
50	49	0.55 ± 0.0030
100	88.4	0.13±0.0140
200	96.1	0.04 ± 0.0010
300	97.6	0.03 ± 0.0005
400	97.7	0.03 ± 0.0032
OKL		
50	23.8	0.77 ± 0.1000
100	60.9	0.45 ± 0.1300
200	88.1	0.17 ± 0.0700
300	91.9	0.08 ± 0.0100
400	93.9	0.07 ± 0.0040
OOL		
50	46.2	0.58±0.1900
100	57.4	0.46 ± 0.0600
200	83.8	0.18 ± 0.0200
300	91.8	0.09 ± 0.0100
400	94.1	0.01±0.0001

Table 2. The inhibition efficiency of mild steel in 1 M HCl solution in the absence and presence of OSL, OKL, and OOL.



Figure 2. The correlation of inhibition efficiency with concentration for all depolymerized lignin products.

3.3 Adsorption isotherm

Adsorption isotherms can provide some supportive information regarding the corrosion inhibition mechanism [49]. In order to investigate the adsorption behavior of OSL, OKL, and OOL in HCl solution, the θ values of weight loss measurement were fitted to various isotherm models such as Langmuir, Freundlich, Frumkin, and Temkin. It was found that all data obtained best fitted to the Langmuir isotherm model (Figure 3). The Langmuir isotherm assumes that only one adsorption site is occupied by adsorbed molecules and there are no interactions with other molecules adsorbed [50]. This isotherm model represents the correlation between θ values and C, inhibitor concentration in the corrosive medium, based on the following relationship [48,50]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$
(7)

where θ is the surface coverage; C_{inh} is the inhibitor concentration, and K_{ads} is the equilibrium constant of the adsorption process. The relation between C_{inh}/θ and C_{inh} at 29 °C is shown in Figure 3, where the linear graphs were obtained. The adsorption parameters, such as regression coefficient R², K_{ads} , and slope values were obtained from the linear fitting plot shown in Figure 3. A very good fit was observed with the regression coefficients R² values of 0.9884, 0.9638 and 0.9936, for OSL, OKL, and OOL, respectively, which indicate a strong adherence to the Langmuir adsorption isotherm. However, the linear line obtained had slopes that deviated from unity (OSL – 0.9098, OKL – 0.7528 and OOL – 0.8696), which contradict from the ideal isotherm plot that is supposed to have a slope of unity and zero intercepts as quoted by [51] from [52, 53]. The departure of the slope values from unity might be due to the mutual interaction of adsorbed molecules in close vicinity, as cited by [54] from [55]. It is also observed from the plots that some points were deviated from linearity which is possibly due to attraction or repulsion between the adsorbed molecules [54]. From the intercepts of the straight lines $(C_{inh}/\theta$ -axis), the K_{ads} value was calculated. The K_{ads} value of OSL was found to be slightly higher than OKL, and OOL signifying that the organic compounds of OSL were adsorbed more effectively on mild steel surface as compared to OKL and OOL [45]. Thus, from the weight loss experiment, it could be concluded that the effectiveness of all depolymerized lignin products as corrosion inhibitors for mild steel in HCl environment are comparable with each other.



Figure 3. Langmuir adsorption plot of mild steel after 24 hr of immersion in 1 M HCl solution in the absence and presence of all depolymerized lignin products.

 K_{ads} calculated from Figure 3 is related to the standard Gibbs free energy of adsorption, ΔG_{ads} , according to the following equation [56]:

$$K_{ads} = \frac{1}{C_{H_2O}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$
(8)

where *R* is the universal gas constant, *T* is the thermodynamic temperature and the concentration of water in the solution is 1000 g L⁻¹) [56]. The ΔG_{ads} value of adsorption process was calculated as -25.63, -22.93 and -23.96 kJ mol⁻¹ for OSL, OKL, and OOL, respectively, at the studied conditions. Generally, the negative value of ΔG_{ads} indicates that the inhibitor is spontaneously adsorbed onto the mild steel surface. Furthermore, the energy values of ΔG_{ads} around -20 kJ mol⁻¹ or less in negative are related to the electrostatic interaction between charged inhibitor molecules and charged metal surface, i.e, physisorption; those of more negative than -40 kJ mol⁻¹ involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type bond i.e. chemisorption [57-60]. From the calculated values of ΔG_{ads} for all inhibitors, it could be assumed that physisorption is the predominating adsorption process on the metal surface.

3.4 Potentiodynamic polarization study

In order to investigate the effect of OSL, OKL, and OOL on the mechanism of cathodic and the anodic reaction of mild steel, a typical potentiodynamic polarization curve (Tafel curve, Figure 4), in HCl in the absence and the presence of various concentrations of OSL, OKL, and OOL was plotted at the room temperature. From Figure 4, it was observed that both the anodic and cathodic branches of the Tafel plot shifts to lower values, at all investigated concentrations when inhibitors were added. These indicated that the organic constituents of OSL, OKL, and OOL inhibited both hydrogen evolution (cathodic reaction) and metal dissolution (anodic reaction) and it is suggested that all inhibitors act as a mixed type inhibitor. Corrosion parameters, such as E_{corr} , I_{corr} , slope of anodic (β_a) and cathodic (β_c) Tafel curves, and polarization resistance values, were determined by extrapolation of anodic and cathodic Tafel polarization curves and listed in Table 3. The observation of Tafel parameters revealed that the addition of inhibitors slightly shifted the E_{corr} values of corrosion reactions; however, the displacement in the E_{corr} values is not showing any specific pattern [61, 62]. The magnitude of β_a and β_c also changed with the increments of the inhibitor concentration; however, the changes were not following any trend. This fact supported the random changes that occurred in E_{corr} values along with the addition of inhibitors [48]. The I_{corr} values listed in Table 3 were used to calculate the inhibition efficiency, $\eta_P(\%)$ based on equation (4). The values of $\eta_P(\%)$ in the presence of OSL, OKL, and OOL reached up to 96.8, 80.9 and 88.0%, respectively, at a concentration of 400 mg L^{-1} . Furthermore, it was also observed that I_{corr} values noticeably reduced with the increase in inhibitor concentration, suggesting that OSL, OKL, and OOL slowed down the corrosion rate of mild steel samples in HCl solutions. Possibly, the organic constituents of OSL, OKL, and OOL were adsorbed on the metal surfaces to form a protective layer on the mild steel electrode, resulting in the decrease of corrosion current values [63, 64]. The polarization resistance (R_p) values and inhibition efficiency based on polarization resistance, $\eta_{PR}(\%)$ which are given in Table 3 increased with the increase of inhibitor concentration signifying that the inhibitors effectively retarded the polarization process at the metal-acid interface; as a consequence, the corrosion process was inhibited [48].





Figure 4. Tafel curves of mild steel in 1 M HCl solution in the absence and presence of (a) OSL, (b) OKL, and (c) OOL.

Table 3. Potentiodynamic polarization parameters for mild steel in 1 M HCl solution in the absence and presence of OSL, OKL, and OOL.

Concentration	E_{corr}	Icorr	β_a	β_c	$\eta_P(\%)$	R_p	$\eta_{PR}(\%)$
$(mg L^{-1})$	(mV,SCE)	$(\mu A \text{ cm}^{-2})$	$(mV dec^{-1})$	$(mV dec^{-1})$	-	$(\Omega \text{ cm}^2)$	-
Blank	-461.0	681.0	63.1	-298.5	-	32.9	-
OSL							
50	-460.0	139.0	63.0	-132.3	79.5	127.6	74.2
100	-459.0	136.0	68.5	-115.9	80.0	130.5	74.8
200	-466.0	43.80	68.3	-102.1	93.6	367.3	91.0
300	-454.0	22.80	53.4	-75.70	96.7	599.6	94.5
400	-449.0	21.50	53.0	-87.80	96.8	616.6	94.7
OKL							
50	-461.0	305.0	86.20	-227.8	55.2	82.8	55.2
100	-458.0	230.0	60.90	-159.6	66.2	85.4	61.5
200	-458.0	219.0	82.60	-158.8	67.8	106.6	69.1
300	-446.0	162.0	54.80	-146.3	76.2	107.1	69.3
400	-456.0	130.0	61.40	-128.0	80.9	137.8	76.1
OOL							
50	-461.0	433.0	72.3	-211.5	36.4	50.83	35.3
100	-458.0	423.0	86.7	-143.8	37.9	53.84	38.9
200	-458.0	325.0	69.3	-164.9	52.2	61.15	46.2
300	-446.0	222.0	71.7	-134.4	67.4	88.16	62.7
400	-456.0	81.60	79.3	-180.0	88.0	285.5	88.8

3.5 EIS measurements

Corrosion of mild steel was evaluated further via EIS measurement. The experiments were carried out at room temperature and the impedance spectra (Nyquist, Bode, and phase angle plots) as shown in Figures 5, 6 and 7 were obtained at the open circuit potential after an exposure period of 30

min in the absence and presence of various concentrations of OSL, OKL, and OOL in 1 M HCl. From the Nyquist plot (Figure 5), it is shown that the electrochemical reaction of mild steel samples appeared in the form of single capacitive loops (semicircles), suggesting that a capacitive layer was formed at the metal-acid interface [48]. It is also observed that in all systems, the semicircles are depressed in nature with the center under the real axis and this may be attributed to the non-ideal capacitive behavior of the electrochemical solid/liquid interface, that deviated from the pure semicircles behavior as the frequency depression that occurred may be due to surface roughness, inhomogeneity of reaction rates on the surface, non-uniform current distribution or varying thickness or composition of protective film during the corrosion process [65, 66]. The impedance diagram in Figure 5 illustrates that the size of the depressed semicircles in the addition of inhibitors are larger than that of the acid solution without inhibitor that increased as the concentration of the inhibitor increased. This indicated that the charge transfer process at the interface was retarded in the presence of inhibitor and consequently the inhibition efficiency increased. All the impedance diagrams were analyzed in terms of the equivalent circuit given in Figure 5(d) to obtain the technical details of impedance spectra and also to calculate various parameters including solution resistance R_s , charge transfer resistance R_{ct} , and constant phase element for the double layer, CPE. A constant phase element (CPE) was used instead of a pure double layer capacitor to compensate for the non-ideal capacitive response of the interface due to the imperfection of the metal surface to a more accurate fit as cited by [67] from [68, 69]. The impedance function of the CPE was related to the double layer capacitance (C_{dl}) and its impedance was described by the expression:

$$Z_{CPE} = Y_o^{-1} \left(j\omega\right)^{-n} \tag{9}$$

where Y_o is the *CPE* coefficient, ω is the angular frequency, *j* is the imaginary number, and *n* is the *CPE* exponent related to the phase shift which signifies surface properties of the working electrode. These parameters can be used to calculate the values of the double layer capacitance (C_{dl}) according to the following equation:

$$C_{dl} = Y_o \left(2\pi f_{\max}\right)^{n-1} \tag{10}$$

where f_{max} is the frequency at which the imaginary component of the impedance is at maximum. The impedance parameters calculated are given in Table 4. From Table 4, it is revealed that the R_s values remain almost unchanged upon addition of inhibitors. The charge transfer resistance, R_{ct} values increased with the increment of inhibitor concentration while C_{dl} decreased. The R_{ct} values of OSL, OKL, and OOL reached maximum values of 628.1, 139.7 and 233.2 Ω cm² respectively, at 400 mg L⁻¹. The capacitance double layer, C_{dl} values decreased from 112 µF cm⁻² (blank solution) to 51.3, 10.9 and 121.4 µF cm⁻² upon the addition of 400 mg L⁻¹, OSL, OKL, and OOL, respectively. The decline of C_{dl} values with the increase of inhibitor concentrations may be attributed either to a decrease in local dielectric constant or to an increase in the thickness of the electrical double layer or both, suggesting that the inhibitor molecules are adsorbed at the metal/solution interface to form a protective

thin layer on the electrode surface [70-71]. It is also noticeable from Table 4 that the CPE parameters, Y_o and n values decreased with the addition of all inhibitors compared to the blank. The value of n that decreased upon the addition of inhibitor might be due to the non-uniform current distribution, where, the current density certainly was perturbed resulting from the adsorption of OSL, OKL, and OOL on the mild steel surface. A similar phenomenon has been observed and reported, but from a different perspective [73-75]. The Bode and phase angle plots illustrated in Figures 6 and 7 showed that the addition of the inhibitor causes the increase in the interfacial impedance, which further increases upon the increment of the concentration of the inhibitor. Furthermore, an aggressive attack of hydrochloric acid corroded the mild steel enormously and made the surface highly uneven, as demonstrated by the small phase angle (Figure 7). The single narrow peak in the phase angle plots indicated a single time constant for the corrosion process at the metal–solution interface. The increment in the peak heights indicated a more capacitive response of the interface due to the presence of inhibitor molecules at the interface that effectively lowered surface irregularities [73].



Figure 5. Nyquist plots for mild steel in the presence of (a) OSL, (b) OKL, and (c) OOL in 1 M HCl, (d) equivalent electrochemical circuit for the fitting of the results.

However, a pure capacitor's behavior was not observed (phase angle $< 90^{\circ}$), which might occur due to the uneven electrode surface or current variation [76, 76]. The inhibition efficiency (η_E %)

values are shown in Table 4. The maximum inhibition efficiency of 98.3, 92.3 and 95.4% can be observed at the maximum concentration (400 mg L^{-1}) of OSL, OKL, and OOL, respectively. These results are in good agreement with the results of weight loss and potentiodynamic polarization experiments.

Concentration (mg L ⁻¹)	$\frac{R_s}{(\Omega \text{ cm}^2)}$	$\frac{R_{ct}}{(\Omega \text{ cm}^2)}$	Y_0 (10 ⁻⁶ Ω^{-1} s ⁿ cm ⁻²)	Ν	C_{dl} (μ F cm ⁻²)	η _E (%)
Blank	4.561	10.81	198.3	0.9149	112.0	-
OSL						
50	4.579	59.93	115.8	0.8781	55.9	82.0
100	4.590	96.97	113.3	0.8615	54.4	88.9
200	4.490	351.8	99.0	0.8379	52.5	96.9
300	4.570	586.0	87.9	0.8461	51.7	98.2
400	4.505	628.1	95.5	0.8200	51.3	98.3
OKL						
50	4.662	27.85	123.4	0.9044	214.2	61.2
100	5.182	29.50	117.4	0.8875	178.9	63.4
200	4.870	40.00	101.9	0.8883	160.1	73.0
300	4.710	76.19	94.3	0.8513	126.0	85.8
400	4.690	139.70	82.9	0.8318	106.9	92.3
OOL						
50	4.662	33.05	127.8	0.8758	185.7	67.3
100	4.674	37.21	124.1	0.8783	183.2	70.9
200	4.748	50.01	159.1	0.8246	182.4	78.4
300	4.631	72.66	141.1	0.8264	170.1	85.1
400	6.248	233.20	62.5	0.9019	121.4	95.4

Table 4. Technical parameters obtained from Nyquist plots at different concentration of G	OSL,	OKL
and OOL for mild steel in 1 M HCl at 29±1°C.		





Figure 6. Bode plots for mild steel with different concentration of (a) OSL, (b) OKL, and (c) OOL in 1 M HCl.



Figure 7. Phase angle plots for mild steel with different concentration of (a) OSL, (b) OKL, and (c) OOL in 1 M HCl.

3.6 HPLC analysis

In order to determine the anticorrosion components of the OSL, OKL, and OOL, the HPLC analysis of test solutions was carried out before and after the corrosion processes of 400 mg L^{-1}

inhibitor. From the HPLC analysis, it was found that OSL, OKL, and OOL contained seven constituents. From this preliminary study, the ratio between the types of phenylpropane units (phydroxyphenyl (H), guaiacyl (G), and syringyl (S)) was estimated as mg g⁻¹%. The ratios of those units for OSL, OKL, and OOL were 12:31:57, 9:38:53 and 9:34:57, respectively. It was also shown that *p*-hydroxyphenyl unit gave the lowest yield as compared to syringyl and guaiacyl units for all depolymerized lignin products. The total yield of H, G, S units for OSL, OKL, and OOL were 85.61, 86.27 and 177.06 mg g^{-1} , respectively. Among the seven constituents present in the depolymerized lignin products, syringaldehyde (S), vanillin (V) and 4-hydroxybenzaldehye (4-HB) have been found to give a significant contribution to the corrosion inhibition of mild steel in 1 M HCl. The concentrations of the three main compounds consumed after the inhibition process from the electrochemical and weight-loss measurement are given in Table 5. Out of the three main compounds that are present in the depolymerized lignin products, only vanillin has been reported as a good corrosion inhibitor for steel and aluminum in various media with the inhibitive performance depending on its concentration [78-81]. It is clearly shown in Table 5, that the percentage of the total consumption of the three main compounds of depolymerized products from the electrochemical study gave a slightly higher percentage as compared to the weight-loss measurement. The amounts of compounds consumed showed a negative correlation with the time of immersion since the higher consumption of the compounds in the corrosion process was recorded by the electrochemical method. This observation is perhaps due to the rapid protonation reaction of the carbonyl group in syringaldehyde, vanillin, and 4-hydroxybenzaldehye to oxonium ion in acidic solutions. Even though this reaction is reversible, for the lesser time of immersion in the electrochemical study, the protonation might be more favorable as compared to the weight-loss method where the protonation reaction and the reversible reactions might be at equilibrium due to the longer time immersion.

		Amount of inhibitor consumption		
Inhibitors	Oxidation Products	Electrochemical	Weight loss	
		study	study	
		%	%	
	4-Hydroxybenzaldehyde	4.02 ± 0.74	3.19±0.52	
OSL	Vanillin	13.00±0.94	9.79±1.09	
	Syringaldehyde	8.18±0.82	6.73±1.16	
	Total	25.20	19.71	
	4-Hydroxybenzaldehyde	6.19±0.91	6.18±0.54	
OKL	Vanillin	9.57±0.64	5.55±0.74	
	Syringaldehyde	9.35±0.61	8.17 ± 0.40	
	Total	25.11	19.90	
OOL	4-Hydroxybenzaldehyde	12.59±0.72	6.49±0.30	
	Vanillin	15.61±0.06	9.17±0.13	
	Syringaldehyde	12.11±0.16	4.46±0.21	
	Total	40.31	20.12	

Table 5. Consumption of main constituents of depolymerized lignin products during the corrosion process by HPLC analysis.

Hence, more compounds are transformed into protonated forms instead of being consumed as neutral compounds in the corrosion process. The total percentage of phenolic aldehyde consumed for all depolymerized lignin products from the weight loss study gave almost the same percentage ranging from 19.71-20.12%, while from the electrochemical measurement the total percentage consumed for all depolymerized lignin products was in the range of 25.11-40.31%. Observation of the results revealed that V showed the highest phenolic monomer to be consumed for all depolymerized lignin, except for OKL from weight loss measurement that showed S was consumed more than the other two phenolic monomers studied. The OOL showed the highest percentage of total inhibitor consumption as compared to OSL and OKL for electrochemical and weight loss measurements of 40.31 and 20.12%, respectively. This might due to the highest total yield of S, G, H units in OOL as compared to OSL and OKL. The consumption of S, V and 4-HB in depolymerized lignin products may vary possibly due to the competition or antagonism effect of other constituents in the mixture. The previous study by [82] suggested that the higher the content of the Syringyl units, which is related to S, the better the inhibitory effect. However, in the present study, it was shown that the highest content of phenolic monomer in the mixture did not necessarily give the higher inhibition effect. In addition, [83] reported that even though caffeine showed the highest content in tea extract, the HPLC results showed that caffeine was not consumed at all in the corrosion process, although caffeine can act as an effective metal corrosion inhibitor when used alone in various electrolytes [84-86]. This report agrees well with the present study, where it was shown that the extent of consumption of S, V and 4-HB did not depend on the total initial concentration of S, V and 4-HB in depolymerized lignin products.

3.7 Surface analysis

The surface morphologies of mild steel surfaces exposed to 1 M HCl solution in the absence and presence of 400 mg L⁻¹ OSL, OKL, and OOL after 24 h of immersion at 302 K were inspected using SEM. The morphology of the mild steel exposed in the blank HCl solution shows a very rough surface (Figure 8b) as compared to the unexposed mild steel (Figure 8a). This is due to the corrosive attack by the acid solution. In the presence of OSL (Figure 8c), the surface is comparatively smoother than the surface of a sample in the blank HCl solution. This indicates that the inhibitor retarded further dissolution of iron; consequently, the corrosion rate of mild steel in 1 M HCl solution was reduced. Meanwhile, the X-ray diffraction diagrams of mild steel sample immersed in 1 M HCl in the absence and presence of the OSL are given in Figure 9. It is noticeable that in the absence of the inhibitor (Fig, 9a) the XRD diagram shows peaks at 27° , 47° and 53° due to the presence of corrosion products of lepidocrocite (γ -FeOOH). Upon the addition of inhibitor, several lepidocrocite peaks have diminished or could have transformed into a thin protective layer indicating that the inhibitors have slowed down the dissolution of iron and protected the mild steel surface from further formation of corrosion products.



Figure 8. SEM image for (a) unexposed mild steel, (b) exposed mild steel in 1 M HCl, and (c) exposed mild steel in 1 M HCl containing 400 mg L^{-1} OSL after a 24 h immersion at 29±1°C.



Figure 9. XRD diagram for (a) exposed mild steel in 1 M HCl and (b) exposed mild steel in 1 M HCl containing 400 mg L⁻¹ OSL after a 24 h immersion at 29±1°C.

4. CONCLUSION

OSL, OKL, and OOL acted as good inhibitors for the corrosion of mild steel in 1 M HCl solution. The inhibition efficiencies increased with the increase of the OSL, OKL, and OOL concentration and in the ascending order of OKL< OOL< OSL for all evaluation techniques. The potentiodynamic polarization studies revealed that the inhibitor affected both anodic and cathodic reactions and acted as a mixed inhibitor. The adsorption characteristic was approximated by the Langmuir adsorption isotherm model for all depolymerized lignin products. The free energy of adsorption indicated that the adsorption of depolymerized lignin products involved mainly physical adsorption. The morphological studies supported the formation of a protective layer over the mild steel surface.

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