Corrosion Inhibition of Thermal Hydrolyzed Lignin on Mild Steel in Hydrochloric Acid

Ebrahim Akbarzadeh

* Young Researchers and Elites club, Science and Research Branch, Islamic Azad University, Tehran, Iran

Abstract

Lignin is an important biopolymer in wood pulping and potentially as great source for wide range of green applications in industry. It is commonly insoluble in water and acidic media, so a thermal acid degradation breaks long polymeric chains and provides the compounds which are soluble. As corrosion inhibitor the hydrolyzed lignin (HL) recognized most effective on mild steel in 1.0 mol hydrochloric acid. The conventional electrochemical techniques have been evaluated at different concentration (75, 150, 300 and 600 ppm w/v) of HL at 25 °C. In addition, the electrochemical tests have been repeated for consideration of chemical stability of inhibitor by following different time of exposure. The conventional electrochemical tests were shown the adsorption of HL molecules onto the metal surface with good inhibition efficiency especially at high concentrations of inhibitor, whereas the %*IE* increased significantly with increasing of immersion time. It can be pertained to functional groups, small molecules and electron sharing of specious which can be adsorbed onto steel surface. The SEM has shown the corrosion reduction after immersion in different time and concentration of HL. Consequently, hydrolyzed lignin could be suitable inhibitor in acidic environments, particularly in 1 mol HCl solution.

Keyword: *Hydrolyzed lignin, Hydrochloric acid, Corrosion inhibitor, Mild Steel, Surface analysis.*

1. Introduction

Corrosion in neutral solutions is different from in acidic media due to the metal surface in acid solutions is oxide free and main cathodic reaction is hydrogen evolution, but in neutral solutions, the surface covered with oxide, hydroxides and oxygen reduction is main cathodic reaction. Inhibitors have always been employed to against corrosion physically, chemically or both. Basically, corrosion inhibitors can be classified into two major groups based on their functionality, cathodic inhibitors can decrease cathodic reaction by precipitation whereas the potential shifts to the negative direction and anodic inhibitors increase the corrosion potential to positive ranges or forcing the metallic surface into passivation. Predominate mechanism of an inhibitor may vary with different factors such as inhibitor concentration, the pH, exposure time, temperature and type of metal. Some organic inhibitors which have lone pair electrons or the π-electrons can interact with the vacant d-orbital of iron atoms at surface and create the barrier layer [1, 2]. The most suitable inhibitors for metals in acid solutions are those contains halide ions, organic compounds (has multiple bonds, especially triple) and elements in group V and VI of periodic table such as oxygen, sulfur or nitrogen.

Lignin is a most abundant bio-polymer which exists in integral part of plants cell walls to strengthening [3]. It produces in pulping processes as by-product or waste material and traditionally burnt as fuel, but nowadays a small amount (2%), commercially used [4]. Lignin has big macromolecule with large molecular weight, so the adsorption of these particles is difficult onto the surface. Many scientists have studied on lignin and proposed several structures, but in all of proposed structures plenty of hydroxyl and carboxyl groups have seen. In softwood lignin, the type of lignin that employed in this study, three monomers were suggested such as: coniferyl moieties (95 %), *p*-hydroxyphenyl alcohol

and the rest sinapyl alcohol [5] moieties (Fig. 1). Lignin-based compound contains plenty

of hydroxyl or methoxy groups that can adsorb onto metal surface and used as corrosion

inhibitors [6, 7]. Lignin is more hydrophobic [8] and insoluble in water specially at the

acidic pH [9], so it is difficult to use it as corrosion inhibitor in acid media. First, it is

needed to have some degradation on its molecular structure by any degradation method

such thermal degradation. The effectiveness of lignin and its modifications as inhibitors is

due to the increasing in the number of OH and COOH groups in the macromolecule [10].

The content of reactive groups such as OH, CO, and COOH was increased by modifying

hydrolyzed lignin with hydrochloric acid [11].
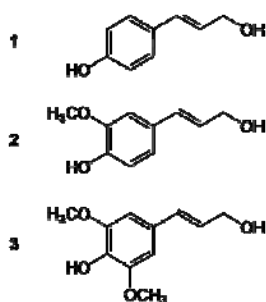
Fig. 1 Three common monolignols: (1) paracoumaryl alcohol, (2) coniferyl alcohol and (3) sinapyl alcohol

In this study, the hydrolyzed Kraft lignin has been achieved from black liquor of empty

fruit bunches of oil palm (BL is the spent cooking liquor contains lignin, hemicelluloses

and residual extractive materials which used in digesting pulpwood into paper pulp). It

was employed as corrosion inhibitor of mild steel in acidic environment. The effects of

two main parameters such as inhibitor concentration and exposure time were investigated

by electrochemical methods on mild steel samples.

2. Experimental

2.1 Materials preparation

Lignin has been extracted from the black liquor (BL) of Kraft pulping of oil palm empty fruit bunch by adding 20% (v/v) sulfuric acid in order to reach pH 2. Lignin was participated in acidic region and then filtered and washed with distilled water of pH 2. It was dried at 45 °C for 3 days and then was ground (<20 μm) carefully.

At further step, lignin was hydrolyzed with concentrated HCl in autoclave at 140°C and liquor ratio was 5:1 (lignin:HCl) for 5 hours. Then reference solution were prepared from 600 ppm (w/v) of hydrolyzed lignin then diluted to reach concentrations of 300, 150 and 75 ppm (w/v). The corrosive solutions for further experiments contain 1 mol HCl and concentration of inhibitor as mentioned previously.

Mild steel samples were used throughout the experiments with the chemical composition as shown in Table 1. The rectangular mild steel coupons of size 2.5 cm×2.5 cm×0.25 cm were used. All reagents used, were prepared from analytical grade and the test solutions for all trials were quiescent and at 25 °C under naturally aerated conditions.

Table 1 Chemical composition (wt %) of carbon steel tested

Element	C	S	Si	P	Mn	Fe
% composition (w/w)	0.2	0.047	0.06	0.039	0.55	remaining

2.2 Potentiodynamic polarization measurements

The potentiodynamic curves were plotted over a potential range of -600 mV to -400 mV with respect to open circuit potential (E_{ocp}) at a scan rate of 1 mV s^{-1} using a conventionally designed three-electrode glass cell of Gamry Potentiostat/Galvanostat (Reference R600^{TM}). Working electrode (Mild steel) adjusted at the bottom of the glass

cell with a holiday of 1 cm^2 as exposure area accompanied by platinum electrode and a standard calomel electrode (SCE) as a counter electrode and reference electrode, respectively. Various corrosion kinetic parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (b_a, b_c) were obtained (Table 2). Corrosion current density can be measured by the intersection of the extrapolated Tafel lines to the E_{corr} of the mild steel electrode. The inhibition efficiency can be calculated from the following equation [12, 13]

$$\%IE = \left[\frac{(i^0_{corr} - i_{corr})}{i^0_{corr}} \right] \times 100 \tag{1}$$

Where i^0_{corr} and i_{corr} are uninhibited and inhibited corrosion current densities, respectively.

Table 2 Polarization parameters of mild steel in 1 mol HCl without and with various concentrations of hydrolyzed lignin.

	concentration (ppm)	E_{corr} (mV vs. SCE)	b_a (mV decade^{-1})	b_c (mV decade^{-1})	I_{corr} (µA cm^{-2})	IE (%)	θ	Corrosion rate (mpy)
Blank	-	-485	66.70	89.20	51.60	-	-	205.5
HL	75	-487	95.3	90	27.2	42.29	0.4729	108.3
	150	-493	99	88	25.4	50.78	0.5078	73.40
	300	-486	85.9	75.5	20.8	59.69	0.5969	60.89
	600	-496	101	91.4	18.2	64.73	0.6473	50.38

2.3 Electrochemical impedance measurements

The impedance measurements were carried out by using the same instrument and Echem analyst software was used for analyzing and calculation of elements in the equivalent circuits. E_{ocp} of sample was measured over 30, 60, 120 and 240 minutes immersing, respectively for various concentration of hydrolyzed lignin and impedance calculated by frequency ranges of 100 kHz to 5 mHz with a signal amplitude perturbation of 10 mV and scan rate of 1 mV s^{-1}. The equivalent circuit was proposed and the values of elements

of the circuit can be measured from Nyquist plots. Different corrosion parameters measured from impedance spectroscopy were tabulated in Table 3.

Table 3 EIS parameters of mild steel in 1 mol HCl with and without various concentrations of hydrolyzed lignin and different time of expossure.

	concentration (ppm)	R_u (Ω cm^2)	R_p (Ω cm^2)	C_{dl} (μF cm^{-2})	IE (%)	θ
Blank	-	0.311	88.6	56.34	-	-
	75	0.829	302.3	36.7	70.69	0.7069
HL, 30 min	150	0.873	433.2	43.1	79.55	0.7955
	300	0.985	552.5	37.8	83.96	0.8396
	600	0.929	559.9	34.2	84.18	0.8418
	75	0.623	187.8	42.7	52.82	0.5282
HL, 60 min	150	0.493	415.3	44.1	78.67	0.7867
	300	0.582	582.4	39.8	84.79	0.8479
	600	0.424	787.7	38.4	88.75	0.8875
	75	0.633	565.6	53.2	84.34	0.8434
HL, 120 min	150	0.692	577.3	49.1	84.65	0.8465
	300	0.517	909.1	47.9	90.25	0.9025
	600	0.489	978.9	46.9	90.95	0.9095
	75	0.518	693.8	50.1	87.23	0.8723
HL, 240 min	150	0.558	755.7	48.0	88.28	0.8828
	300	0.645	917.1	46.7	90.34	0.9034
	600	0.592	1024.3	47.3	91.35	0.9135

Results and Discussion

3.1 Hydrolyzed Lignin versus Native Kraft Lignin

Hydroxylation provides the large number of carboxyl groups in the compound which helps to better water solubility. In this study, diluted hydrochloric acid was utilized for treatment of the Kraft lignin. The FTIR spectra of native and hydrolyzed lignin treated were showed in Fig. 2, whereas lignin has a broad band at 3400 cm^{-1}, attributed to hydroxyl groups in phenolic structure and hydrolyzed lignin spectrum shows a high intensity phenolic OH band at 1375 cm^{-1} and the intensities of CH vibration of methoxyl

group decreased at 2920-2810 cm^{-1}. The thermal hydrolysis treatment also increases the intensity of C-OH band at 1047 cm^{-1}. The intensity of C=C of aromatic ring band at 1680 and 1605 cm^{-1} is highly affected by the treatment of lignin with hydrochloric acid.
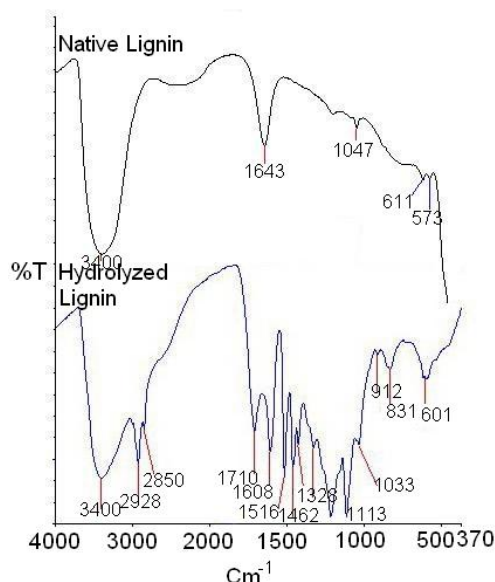
Fig. 2 FT-IR spectra of native and hydrolyzed lignin (HL) samples of Kraft lignin

3.2 Open circuit potential versus time of immersion

The variation of open circuit potential (OCP) of working electrode versus of exposure time is important definition of corrosion domains and determining probable inhibition [14].

Fig. 3 represents the variation of the OCP of the mild steel electrode with time passed (seconds) in aerated non-stirred solutions 1M HCl solution in absence and presence of various concentrations of hydrolyzed lignin (HL) at 20 °C. Corrosion potential E_{corr} at steady-stat in absence of inhibitors are always negative than potential of immersion at $t = 0$ due to dissolving of oxide film formed onto the metal surface and the attack on the bare metal [15]. The steady-state potential can be achieved over 2 hours of immersion. Addition of various concentrations of HL can shift the E_{corr} at steady states to more

positive direction; indicate that they absorb onto the metal surface and prepare a stable Fe-complexes as a barrier and protective layer, while the general features of the potential–time curve did not change. Moreover, increasing the additive concentration improves this effect (300 ppm and 600 ppm). The OCP curve commonly decreases to a minimum value, as result of balancing of protective film formation-dissolution rate. The trends of blank and 75 ppm and 150 ppm of inhibitor are similar and the potential increased with increasing of inhibitor concentration. After a certain time, depending on HL concentration, the potential declined to reasonably steady values. For two highest amount of inhibitor (300 and 600 ppm) the initial potential adjusted positively and reduced to steady state values remarkably. It has been shown that the highest concentrations were more capable to form a barrier layer and reach to steady state quickly. This trend investigated two processes, first is the formation of inhibitive protective layer onto the electrode surface followed by shifting the OCP values to noble region (positive potential), and second process is corrosion, which reduce potential towards active region and then become steady while reach to balance.
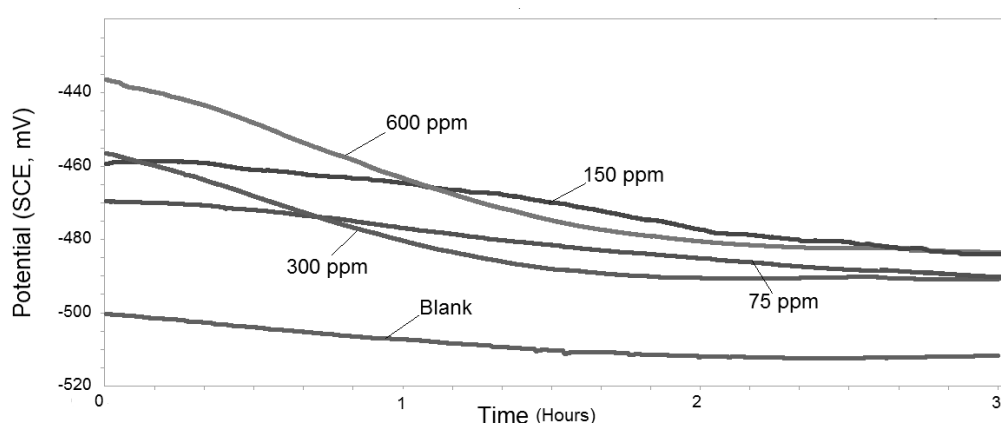

Fig. 3 Open circuit potential curves of mild steel in 1 mol HCl for different concentration of hydrolyzed lignin

3.3 Potentiodynamic Polarization

As shown in Fig. 1, Lignin consists of polyphenolic monomers which can be adsorbed onto the metal surface due to presence of electron donating groups. Polarization curves for mild steel in 1 mol HCl at various concentrations of hydrolyzed lignin (HL) are presented in Fig. 4. The values of corrosion current densities (i_{corr}), corrosion potential (E_{corr}), cathode and anodic Tafel's slopes and inhibition efficiency (%IE) as function of HL concentrations was calculated from the polarization curves and presented in Table 2. Tabulated values revealed that corrosion current decreased prominently, so inhibition efficiency increased with increasing inhibitors concentration. The presence of inhibitor shifted the E_{corr} to both cathodic and anodic direction; it could be investigated as mixed-type mechanism for inhibition. Anodic Tafel slopes changed slightly. Commonly, if only the displacement in E_{corr} is over than 85 mV the inhibitor can be seen as a cathodic or anodic type inhibitor [16] otherwise, when displacement of E_{corr} is lower than 85 mV, the inhibitor can be supposed as mixed type which was observed from the results.
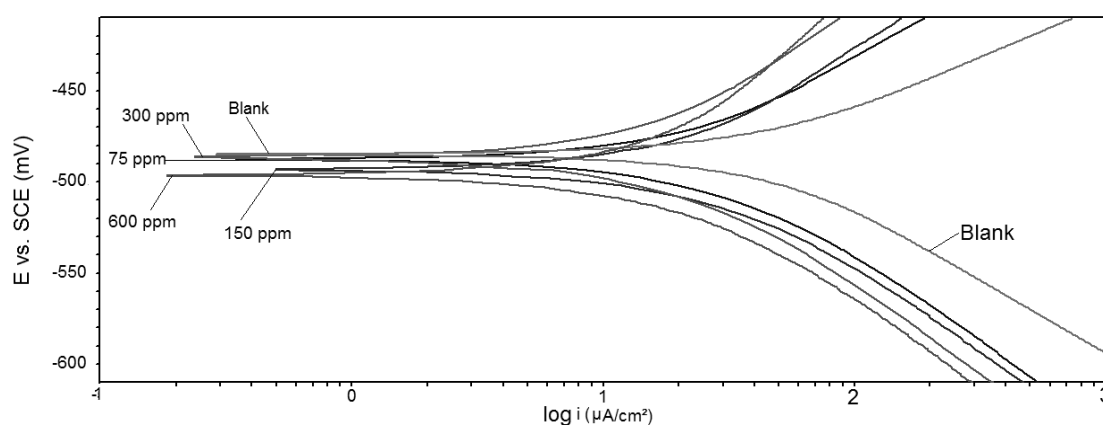

Fig. 4 Polarization curves of mild steel in 1 mol HCl with different concentration of hydrolyzed lignin

It can be assumed that the active site of inhibitors such as functional groups with donating electron cooperated for formation of a protective film rather than a simple adsorption on the electrode surface. This would reduce current density without changing the anodic slope, but the organic adsorbed film seems to inhibit effectively when the metal dissolution reaction at the corrosion potential effectively as well as in its vicinity [17]. The reaction rate between formation and dissolution of barrier layer will be balanced after a certain time passing over immersion in corrosive media with presence of inhibitor. For instance, the electron transfer can be expected with inhibitors having relatively loosely bound electrons [18].

In Fig. 4, the polarization curves of HL are shifted towards lower current density values and results show that the reduction of i_{corr}, can be attributed to the molecular structure and functional groups. The inhibitor adsorbed onto the metal surface and retards the anodic or cathodic reaction or both proved by reduction in current density or changing the Tafel slopes in polarization curves. It has been reported that the effectiveness of lignin and its modifications as inhibitors is due to increasing in number of OH and COOH the macromolecule or monomers of lignin [15, 19]. Consequently, hydrolyzed lignin showed good inhibition efficiency (%IE between ranges of 40 to 70) based on chemisorption mechanism of adsorbing and electron sharing but it was under controlling of dissolution rate of barrier film and inhibition strongly depend on stabilization of protective film. Moreover, this inhibitor was first adsorbed onto steel surface and therefore impedes by blocking the reaction sites without affecting the anodic and cathodic reactions, resulted with no change in the anodic and cathodic Tafel slopes.

3.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance measurements were examined at four levels of immersion time 30, 60, 120 and 240 minutes over the frequency range at open circuit potential for blank and inhibited solution samples at various concentration of HL. The Nyquist plots are presented in Fig. 5 and the simple equivalent circuit CPE was employed for modeling and calculation of corrosions parameters. Different times of immersion were helpful to determining and investigation of time factor on inhibition efficiency of HL in this media.
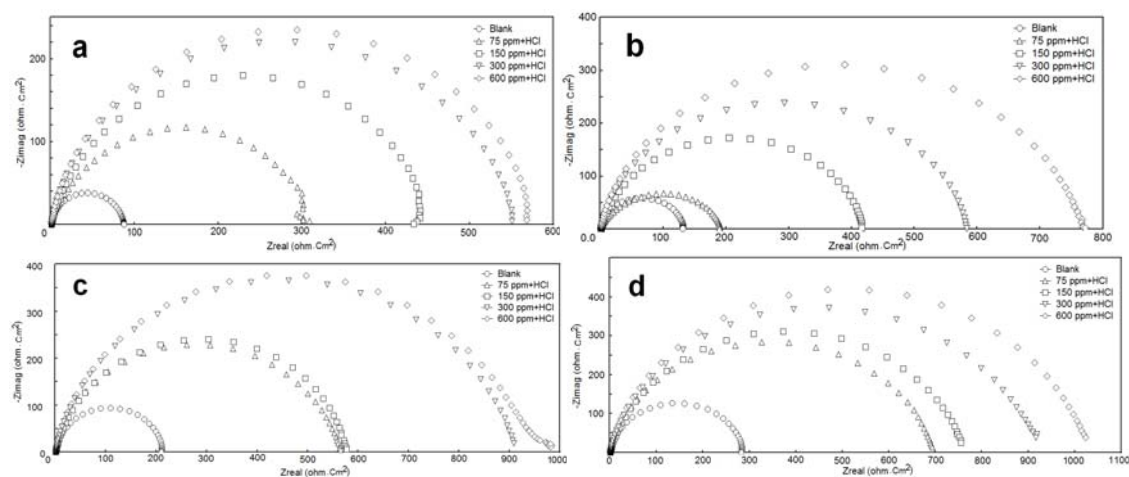
Fig. 5 EIS curves of mild steel in 1 mol HCl with 0, 75, 150, 300, 600 ppm of hydrolyzed lignin as inhibitor at (a) 30 (b) 60 (c) 120 (d) 240 minutes immersing time, respectively.

The impedance spectra of all samples for mild steel in 1 mol HCl are similar in shape at high and low frequencies which are capacitive loop and inductive loop, respectively. The capacitive loop was attributed to the charge transfer and formation of surface film which produce the ohmic resistances of the corrosion product [20] whereas slight inductive loop associated with the relaxation process followed by adsorption species like H_{ads}^{+} on the electrode surface [21]. The equivalent circuit (Fig. 6) with a constant phase element (CPE), is used to fit our experimental results [22, 23]. It shown the Nyquist diagrams

represented electrical equivalent circuit elements that used for calculation R_s electrolyte resistance, R_{ct} the charge transfer resistance or resistance of protective surface film with C_{dl} as the double-layer capacitance. The increasing of R_{ct} values improves the inhibitory action and increases the inhibition efficiency calculated and shown with the other impedance parameters in Table 3. Polarization resistance values increased from 88.6 Ω cm^2 for blank sample to the maximum 560, 787.7, 978.9 and 1024.3 Ω cm^2 for highest concentration of each immersing time of 30, 60, 120 and 240 minutes, respectively.
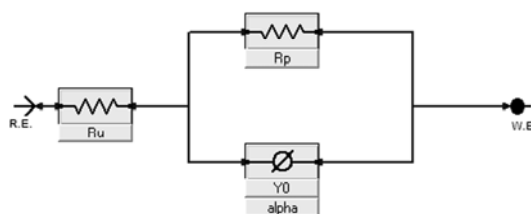
Fig. 6 Equivalent circuit used to fit the impedance measurements via Echem Analyst software

The C_{dl} values decreased from maximum value for blank sample to lower ranges by the increasing of the HL inhibitor concentrations, respectively. It can be seen clearly that higher hydrolyzed lignin concentration and much immersion time in corroding solutions led to better inhibition of mild steel in 1 mol HCl solution while the inhibition efficiency %*IE* reached to more than 70%. Inhibiting effects of hydrolyzed lignin of mild steel could be proved more effective than native lignin and/or monomers of lignin as have been studied [15, 19]. The decrease in C_{dl} values indicates that the adsorption of degraded HL molecules on the metal surface cause to increasing in the thickness of the electrical double layer and reduction of local dielectric constant in absence of polar water molecules. First, inhibitors must be adsorbed onto the metal surface, which is oxide-free

in acid solutions then retard the cathodic and/or anodic corrosion reactions. In acid solutions, the inhibitors interact with metal surface in different ways which can occur simultaneously beneath of experimental conditions. It is difficult to assign a single mechanism when some of different factors such inhibitor concentration, pH of acid, temperature, nature of acid anion or presence of other specious interacted. Functional groups may affect vary on corrosion inhibition in organic inhibitors, in addition same functional groups provide different effects due to the molecular structure on the electron density and size of the hydrocarbon portion in the molecule. Higher charge resistances especially at higher concentrations than blank sample have shown the inhibition effects in each immersing period and this trend continued curves in Fig. 5 that diameters of the capacitive loop increased with increasing inhibitor concentrations due to the enhancement of metal surface covering by metal-organic protected film replaced by water molecules. Therefore, the C_{dl} values decreased with reduction in local dielectric constant and/or increasing in the thickness of the electrical double layer [24]. Consequently, the indicated capacitive loops in all plots at high frequencies in the absence and presence of HL, signifying that the corrosion process is mainly controlled by a charge transfer process. The two steps corroding process suggested as, oxidation of metal or anodic dissolution and then relaxation process followed by the corrosion products adsorption which contain inhibitor molecules or redissolution of protective film at low frequencies onto the metal surface [25]. The capacitive loop diameters increased by increasing of HL concentrations, which attributed to high coverage of metal sample surface by inhibitor. Generally, adsorption of inhibitors to form the protective film enhanced the electrical resistance and provides protection against corrosion.

3.5 Adsorption isotherm

Inhibitors play the role in two different methods: physically by introducing a physical barrier to the ions or molecules immigration to/from the metal surface (or electrostatic adsorption at lower activation energy) [18]; or chemical blocking the anodic/cathodic reactions by actual charge sharing with higher activation energy and slower than physisorption. Most of organic inhibitors are chemisorbed inhibitors on metal surface [26]. Metal/organic compounds were adsorbed to form an impermeable protective film and shielding it from the corrosive media. The degree of surface coverage (θ) was calculated using the following Equation [27]:

$$\theta = 1 - \frac{i_{corr}}{i_{corr}^0} \qquad (2)$$

The corrosion inhibition pertained to adsorption rate of lignin, so for this reason the degree of surface coverage (θ) obtained from EIS values (Table 3) calculated for hydrolyzed lignin in 1 mol HCl. Some parameters of organic molecules such as molecule size, type and number of functional groups, polarity were investigated to have higher rate of adsorptions. Langmuir suggested the relation for adsorption process of inhibitor compounds on the metal surface [28]

$$\frac{\theta}{1-\theta} = K_{ads} C_{inh} \qquad (3)$$

Where θ is the surface coverage coefficient, K_{ads} is the equilibrium constant of the adsorption, C_{inh} is the inhibitor concentration. At first, a molecule of HL adsorbed physically via Van der Waals forces and is further stabilized through chemisorption to form a loose bonding with lone pair electrons or π-electron. The values of free-energy of adsorption were calculated by Langmuir's isotherm which is well fitted data with the

highest regression coefficient close to 1 was obtained as can be seen in Fig. 7. It shows

the linear curves when $\theta/(1-\theta)$ versus C_{inh} were plotted at and the linear equation and

regression distribution. This linear trend confirms that HL obey Langmuir's adsorption

isotherm. The value of the adsorption–desorption equilibrium constant, K_{ads}, was

determined from the slope of the isotherm line (L mg^{-1}). It can be seen from Fig. 7 that

has the highest adsorption ability belong to the samples which immersed longer (240, 120

or 60 minutes) relatively same slope or K_{ads} but in shortest time of immersion, loose

bonding or low adsorption existed due to the lowest equilibrium adsorption constant. The

plotted results were exhibited linearly with very good correlation coefficients. It could be

suggested that the adsorption of the inhibitors on anodic sites by chemical adsorption and

adsorption on cathodic sites due to the electrostatic attraction.
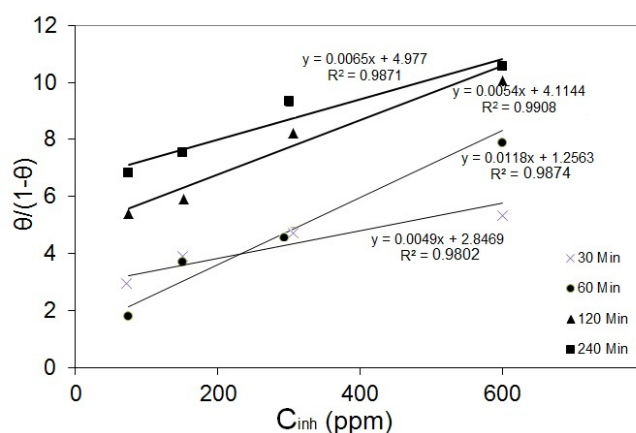
Fig. 7 Langmuir adsorption plot for mild steel at 1 mol HCl and presence of hydrolyzed

lignin at different concentrations and immersed for 30, 60, 120 and 240 hours

3.6 Surface morphology analysis

In Fig. 8, surface morphology of corroded samples in blank (a), 300 ppm, 60 and 240

minutes (b, c) and 600 ppm, 60 and 240 minutes (d, e), respectively were shown. The

effect of inhibitor and corrosion rate can be investigated by their comparison. Highest corroded surface was investigated from (a) which shows the pitting and oxidation. Whereas, in Fig. 8 (b, c) at the presence of HL in medium concentration, some protection and inhibition can be found, it will be increased with increasing time of immersion by higher degree of HL adsorption. The highest degree of protection of HL in HCL solution were exhibited at Fig. 8 (e) with less amount of surface degradation such as pitting and precipitated organic compound can be seen in brightness area. Generally, based on the anodic and cathodic site onto the metal surface the degree of protection/corrosion will be changed. The stabilization of protecting film on the surface depends to the rate of formation and dissolution of barrier film which finally affected on corrosion efficiency.
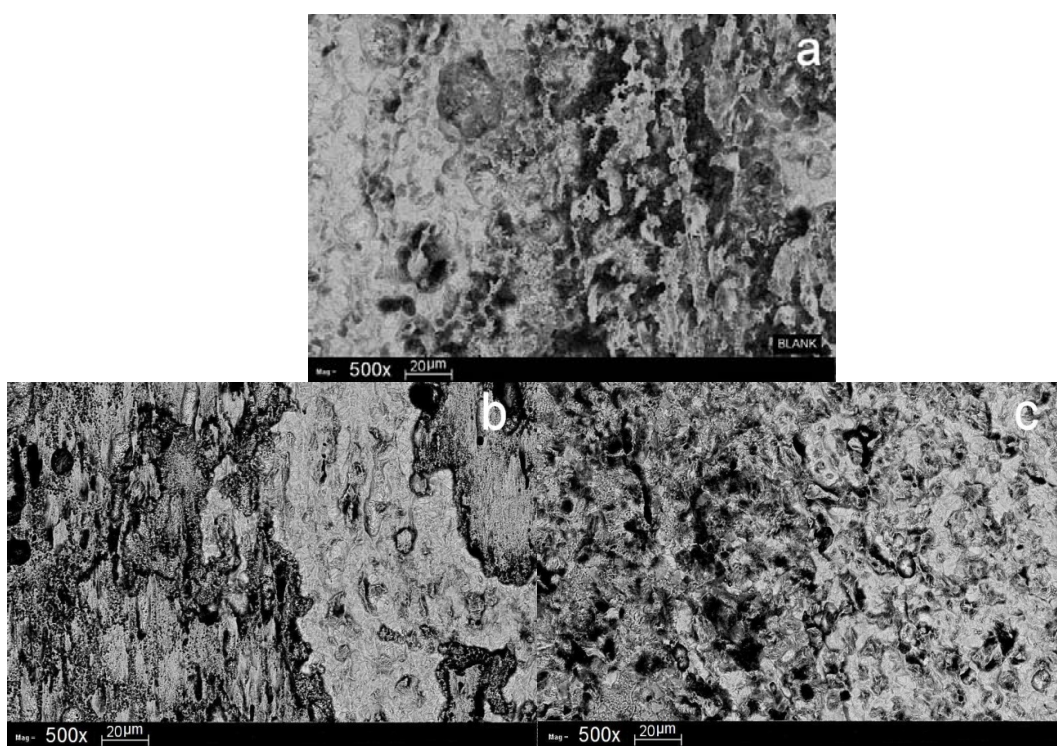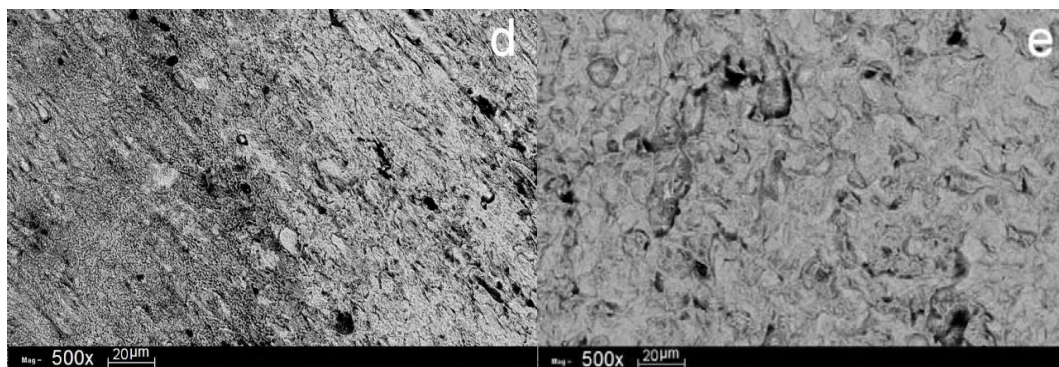
Fig. 8 SEM micrographs of corroded mild steel immersed in 1 mol HCl without inhibitor (a); 300 ppm, 60 and 240 min. (b, c) and 600 ppm, 60 and 240 min. (d, e)

4. Conclusion

- Hydrolyzed lignin could be suitable inhibitors for mild steel corrosion in 1 mol HCl at 25 °C with average efficiency of 80% especially at higher concentration and longer time. The HL exhibited better inhibition due to small molecules than native lignin polymer chain and large number of hydroxy and methoxy functional groups.

- The time is an important parameter for the best inhibition efficiency of HL. Timing period is necessary regarding to equilibrium rate for formation and dissolution reactions of protective film onto the metal surface. More immersing time led to better inhibition of HL molecules to overcoming of any disturbing effects in corrosive solution. The small molecules of degraded lignin molecules need time for relaxation.

- It is confirmed that HL are mixed type inhibitors from the polarization study and they obey Langmuir's adsorption isotherm in HCl solution at 25 °C.

- Scanning Electron Microscopy confirms that the structural morphology of mild steel is less corroded in a solution containing higher HL concentration especially compared to the solution which in absence of inhibitor.

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