Corrosion Inhibition Performance of Lignin Extracted from Black Liquor on Mild Steel in 0.5 M H₂SO₄ Acidic Media

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Abstract

In this study, lignin, a polyhydroxy compound, was extracted from black liquor of pulp and paper industry, and characterized. In view of the potential of such polyhydroxy compounds to adsorb onto metal surfaces, the corrosion inhibition efficiency of lignin on the corrosion of mild steel by 0.5 M H₂SO₄ has been studied using weight loss method, electrochemical polarization and impedance methods. The morphological changes of the surface during corrosion, in the presence and absence of the inhibitor, were studied by scanning electron microscopy. Results of these studies show that lignin does inhibit the corrosion of mild steel by sulfuric acid, and that the inhibition efficiency increased with lignin's concentration.

Keywords: corrosion inhibitor, black liquor, lignin, polarization, impedance.

Introduction

Loss in terms of money and material, as a result of metal corrosion, is a serious matter of concern in any industry, for which corrosion prevention and control is very much necessary. As steel, an important and widely used material at any given industrial sector, is highly prone to corrosion, it needs to be protected, which is a challenging task for scientists and engineers [1, 2, 4]. Corrosion protection using inhibitors is one of the easiest, economic and effective methods, for which many inorganic compounds are found suitable [7]. However, due their heavy costs and toxicity, focus has shifted towards the search of naturally occurring, organic and eco-friendly compounds of corrosion inhibitors, with their added advantages of being safe, ready available, economic and renewable [8]. The presence of hetero atoms such as phosphorous, sulphur, nitrogen or oxygen is the main condition for organic compounds to act as corrosion inhibitors. Lignin, a phenolic polymer, is one of the suitable materials for the said purpose [13, 14], as it is the second most abundant natural polymeric material, after cellulose. Lignin is present in the plant cell wall, from the combination of

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hemicellulose and cellulose. It acts as reinforcement for the lignocellulosic matrix, and provides rigidity, water-impermeability and resistance against microbial attacks [5, 6].

Figure 1. Lignin extraction of black liquor from pulp and paper mills.

Lignin is available from plants, ranging between 15% and 34% in mass [9]. Lignin worldwide production reaches up to 50-60 million tons per year, as a non-commercialized waste product. It is a phenolic polymer primarily derived from three hydroxycinnamyl alcohols or monolignols, namely p-hydroxyphenyl, guaiacyl and syringyl, as shown in Fig. 1. Free radical coupling reactions of these monolignols respectively yield guciacyl, syringly and p-hydroxyphenyl units [11, 12]. Thus, lignin contains various functional groups such as -OH, -RCOOH and –ROCH$_3$ groups (Fig. 1) that can adsorb onto a metal surface by sharing their lone pair of electrons with the free d-orbital of a metal, a property that may be effectively utilized for corrosion control. Though one can find quite a few reports on the use of lignin (modified and unmodified), obtained from various sources, as an effective inhibitor for mild steel corrosion, the corrosion media are restricted to either 3.5% NaCl or HCl. Studies on the corrosion inhibition effect of lignin on sulphuric acid are scarce, however, they are as important as interesting, since H$_2$SO$_4$ is widely used in petrochemical processes, acid pickling, refining, and industrial cleaning, with mild steel as the base material [1, 2, 3]. Also, since the adsorption of inhibitor molecules onto the surface of a substrate depends on the chemical nature of the inhibitor molecules, type of electrolyte and charge on the metal surface, lignin obtained from different sources is bound to have different chemical compositions and interactions with the surrounding electrolytes and the metal surface. In view of this, the present study aims to explore the inhibitive potential of lignin, obtained from black liquor, on the corrosion of mild steel, in a H$_2$SO$_4$ solution at its different concentrations, using weight loss, electrochemical techniques of potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) analysis. Scanning electron microscopy is used as a tool to look at surface morphological changes occurred during polarization studies, with and without inhibitor.

Experimental
The black liquor was collected from pulp industry in north Karnataka, and lignin was extracted using a standard procedure. After collection, black liquor was filtered to remove unwanted materials, then it was heated at 80 ℃ for four hours, after which the solid content was about 70-80%; following that, 0.5 M sulfuric acid was slowly added, to adjust to pH 2, and lignin was precipitated out, repeatedly washed with Milli-Q water, and it was dried overnight in an oven at 70 ℃.
Mild steel with the composition C=0.337wt%, Si=0.163wt%, S=0.0464wt%, P=0.053wt%, Fe–balance, was used as substrate in all essays. It was cut into rectangular pieces of uniform size, which were degreased using emery paper and ethanol, thoroughly washed with distilled water, sonicated in ethanol for 20 minutes, and dried in an oven. Solutions containing different concentrations of lignin (100-1000 ppm) were prepared in AR grade 0.5 M sulfuric acid, with various concentrations of lignin at room temperature. The weight loss of mild steel specimens was determined after 30, 60, 90, 120, 150 and 180 minutes. The percentage inhibition efficiency (IE %) and the degree of surface coverage (θ) for different concentrations of lignin (100 to 1000 ppm) was calculated using the following formula:

$$IE\% = \frac{W_0 - W_i}{W_o} X100 \qquad (1)$$

$$\theta = \frac{W_0 - W_i}{W_o} \qquad (2)$$

where W_0 and W_i are the weight loss values, respectively in the absence and in the presence of the inhibitor.

Polarization studies
Polarization experiments were conducted using a three electrodes assembly, with mild steel as the working electrode (fixing the exposed surface area of the specimens at 0.25 cm^2), a platinum gauze as the auxiliary electrode and a silver-silver chloride electrode as the reference electrode. All the measurements were carried out under unstirred conditions at ambient temperature, using a CH instrument (660E). Initially, open circuit potential (OCP) was measured for 30 minutes, and then the polarization studies were carried out between ±250 mV of OCP. The inhibition efficiency (IE %) was calculated using the following relation:

$$IE\% = \frac{I_{Corr} - I_{Corr(i)}}{I_{Corr}} X100 \qquad (3)$$

where I_{Corr} and $I_{Corr(i)}$ are the corrosion current densities, respectively without and with the addition of the inhibitor.

Electrochemical impedance spectroscopy
Under above mentioned similar experimental conditions, impedance measurements were carried out after measuring the OCP for thirty minutes. The

Nyquist plots were 12 points per decade, and the frequency ranged from 10 KHz to 1 Hz; with 5 mV amplitude of sine wave at OCP, they were obtained in the absence and with different concentrations of the inhibitor. The equivalent circuit was proposed, and the values of the circuit elements were obtained using the software available with a CH instrument. From R_{ct} value or polarization resistance, the inhibition efficiencies were calculated by the following equation [16]:

$$IE\% = \frac{R_{Ct(i)} - R_{Ct(o)}}{R_{Ct(i)}} \times 100 \tag{4}$$

where $R_{Ct(i)}$ and $R_{Ct(o)}$ represent the charge transfer resistance, respectively in the absence and presence of the inhibitor.

SEM Analysis
The surface morphology of mild steel specimens was analyzed by SEM (VEGAJ TESCAN). Images were obtained for cleaned mild steel specimens, before and after polarization studies, both in the presence and absence of the inhibitor.

Results and discussion
Weight loss measurement
Weight loss measurements, for the determination of corrosion rates and inhibition efficiency, are a non-electrochemical method, and they provide more practical results than the electrochemical method, as the experimental conditions are approached in a more realistic manner, even though the study requires more time. Therefore, non-electrochemical results may quantitatively differ from electrochemical results. The calculated inhibition efficiencies and surface coverage at different concentrations of lignin are presented in Table 1. From the results, it is clear that, as the concentration of the inhibitor increased, the surface coverage increased, leading to better inhibition efficiencies and, consequently, to lower corrosion rates. The inhibition efficiency was found to be the highest at 1000 ppm of lignin, above which there was no appreciable change, either in the surface coverage or in the inhibition efficiency.

Table 1. Weight loss data for mild steel in 0.5 M sulfuric acid at various concentrations of lignin after 3 hours of immersion.

Concentration (ppm)	% IE	Θ
0	-	-
100	42	0.4276
200	43	0.4318
300	57	0.5703
400	56	0.5600
500	59	0.5901
1000	76	0.7643

In Fig. 2, weight losses of the specimens at different time intervals and for different concentrations of lignin are presented.
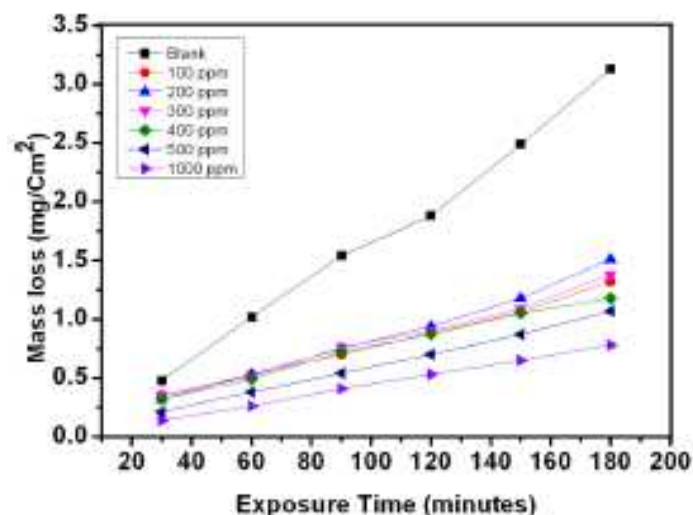
Figure 2. Weight loss in mg vs. exposure time in minutes for mild steel in sulfuric acid.

As expected, in the absence of lignin, a continuous increase in weight loss was observed at all intervals of time, while in the presence of lignin, weight loss was considerably reduced at all concentrations and at all time intervals. Therefore, it may be expected that, with an increased number of lignin molecules, more sites on the metal surface get covered by those molecules, and get saturated around 1000 ppm of lignin. Also, at higher concentrations of lignin (above 400 ppm), the corrosion rate is almost uniform at different time intervals, indicating better and maximum surface coverages at these concentrations, even when they are exposed to lignin solutions for higher time intervals. Hence, it seems to be required an optimum concentration of lignin to get better corrosion inhibition results.

Polarization studies
Polarization curves for mild steel in a 0.5 M H_2SO_4 solution, in the absence and presence of different concentrations of lignin, are shown in Fig. 3.
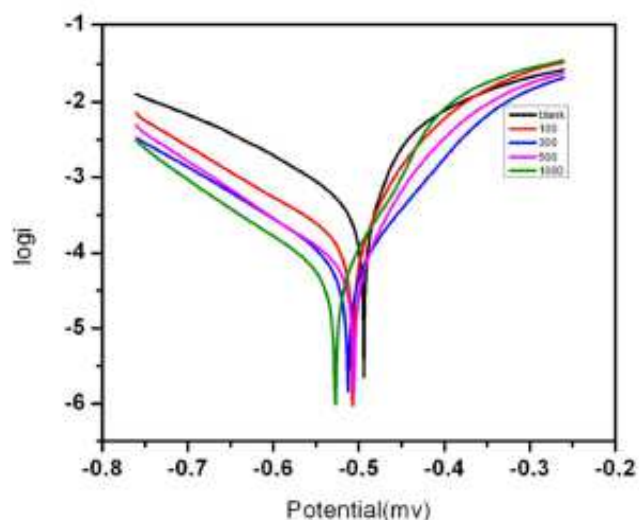

Figure 3. Tafel polarization curves for a mild steel specimen immersed in 0.5 M H_2SO_4, in the absence and presence of lignin's different concentrations.

Electrochemical parameters obtained from polarization curves, i.e., corrosion potential, corrosion current, anodic and cathodic Tafel slopes, % IE, and degree of surface coverage, are presented in Table 2.

Table 2. Polarization parameters of mild steel in 0.5 M H_2SO_4, without and with various lignin's concentrations.

Concentration (ppm)	E_{corr}	I_{corr}	β_a(mV dec^{-1})	β_c(mV dec^{-1})	%IE	θ
0	-492	7.6×10^{-4}	124	69	-	-
100	-507	1.575×10^{-4}	110	71	58	0.58
300	-512	1.803×10^{-4}	109	63	76	0.76
500	-505	2.641×10^{-4}	105	67	88	0.88
1000	-528	3.237×10^{-5}	90	73	95	0.95

As it can be seen from the figure and the table, the anodic and cathodic branches of the polarization curves, in the presence of lignin, are shifted towards lower currents. The extent of decrease in cathodic currents is predominant, compared to anodic currents, suggesting a higher inhibition of cathodic reactions (hydrogen or oxygen reduction), in the presence of lignin, accompanied by a weaker inhibition towards the anodic dissolution of mild steel. The maximum inhibition was observed at the concentration of 1000 ppm, which is in good agreement with the above discussed weight loss measurement. The shift in the corrosion potentials towards more negative values, in the presence of the inhibitor, is further suggestive of the inhibition of cathodic reactions.

Electrochemical impedance spectroscopy (EIS)

Fig. 4 shows the Nyquist plots for mild steel in 0.5 M sulfuric acid, respectively without inhibitor, and in the presence of different concentrations of lignin. Circuit parameters obtained by fitting the data with a suitable circuit are used to analyze the impedance data. A simple equivalent circuit, as shown in the inset circuit in Fig. 4, is used to fit the Nyquist plots, both in the presence and absence of the inhibitor. It consists of solution resistance (Rs), charge transfer resistance (Rct) and one constant phase element (CPE). CPE was employed instead of the double-layer capacitance (Cdl) to describe the heterogeneity in the system.

The charge transfer resistance associated with the electrochemical reaction at the interface was much lower in the absence of the inhibitor (see Table 3), indicating the ease of a corrosion reaction [13]. However, when lignin was adsorbed onto the metal surface, the charge transfer resistance increased, leading to a decrease in corrosion. The inhibition efficiency increased with an increase in lignin's concentration, suggesting a higher and better inhibitive (or passive) surface modification of mild steel, due to the adsorption of more lignin molecules onto the surface, hindering the electrochemical corrosion process [14].
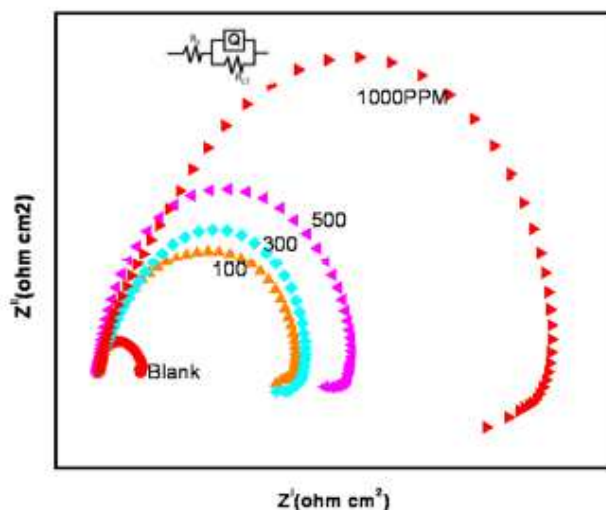
Figure 4. Nyquist plot of mild steel specimen in different concentrations of inhibitor.

Table 3. EIS parameters of mild steel in 0.5 M H_2SO_4 without and with various concentrations of lignin.

Concentration (ppm)	Rct Ohm cm^2	%IE	Θ
0	31.93		
100	136.40	76	0.76
300	145.20	78	0.78
500	176.40	81	0.81
1000	313.10	89	0.89

SEM analysis

The scanning electron micrographs of mild steel, before and after polarization in sulphuric acid, are presented, respectively, in Fig. 5a and b.
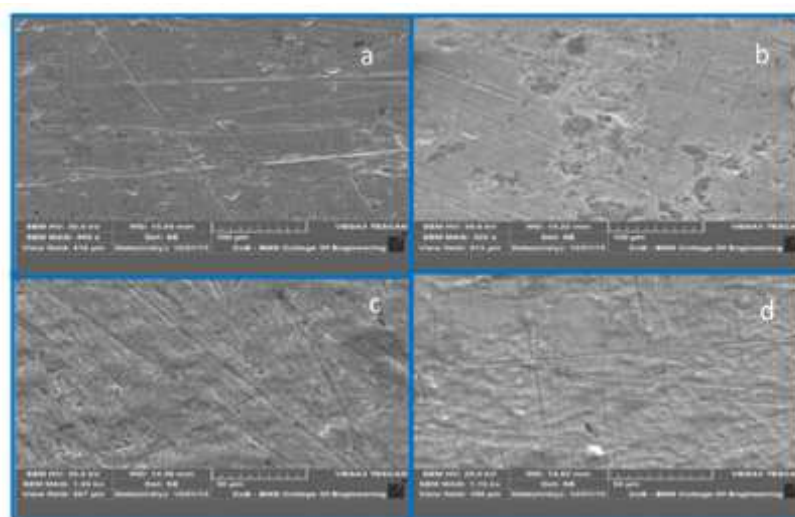

Figure 5. SEM images of **a**) mild steel, **b**) mild steel after polarization in H_2SO_4, **c**) mild steel after immersion in H_2SO_4 with lignin for 30 minutes, and **d**) mild steel after polarization in H_2SO_4 with lignin.

It is very clear from the image (Fig. 5b) that, after polarization, a large number of pits was formed on the surface of the mild steel, due to its corrosion by the acid. While Fig. 5c is the micrograph after adsorption of the inhibitor onto the mild steel surface, Fig 5d is the surface morphology observed after polarization of mild steel in a solution of lignin in 0.5 M sulfuric acid. In Fig. 5d, pits are hardly observed, because of the inhibition action of lignin towards the corrosion of mild steel by acid.

EDS mapping for carbon and oxygen (main elements in lignin) given in, respectively Fig. 6a and b, on the mild steel surface, suggests uniform adsorption of the inhibitor onto the substrate's surface.
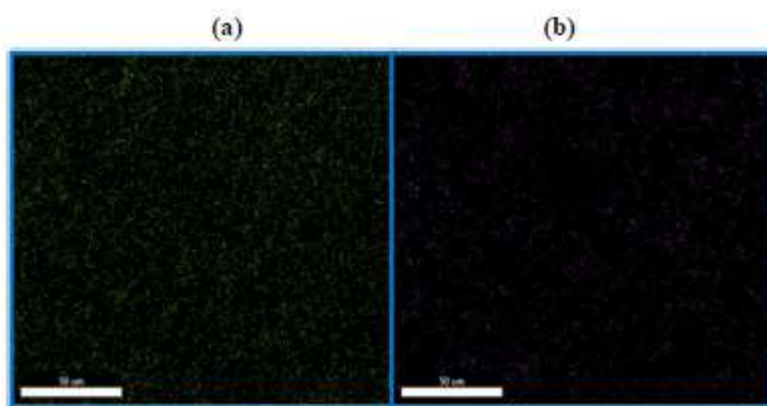

Figure 6. EDS mapping a) carbon b) oxygen.

Conclusions

The aim of the present study was to investigate the inhibition efficiency of low cost, eco-friendly lignin, obtained from black liquor of pulp and paper industry, on mild steel corrosion by sulfuric acid. Based on the results of this study, it can be claimed that lignin effectively adsorbs onto the surface of mild steel, making it less prone to corrosion, even in acidic environments. The corrosion inhibition efficiency increases with an increased concentration of lignin, up to 1000 ppm, due to increased adsorption. However, very high concentrations of lignin may result in an increased competency between the lignin molecules and adsorption sites, leading to an inefficient adsorption, and thereby causing a reduction in inhibition activity.

References

1. Hussin MH, Kassim MJ, Razali NN, et al. Arab J Chem. 2016;9:s616.
2. Lebrini M, Legrenee M, Vezin H, et al. Corros Sci. 2007;49:2254.

3. Benali O, Benmehdi H, Hasnaoui O, et al. J Mater Environ Sci. 2013;4:127.
4. Srivastava V, Singh MMJ. Appl Electrochem. 2010;40:2135.
5. Robert D, Bardet M, Lapierre C, et al. Technol. 1988;22:221.
6. Li H, Saeed A, Ni Y et al. Chem Technol. 2010;30:48.
7. Banera MJ, Caram JA, Gervasi CA, et al. J Appl Electrochem 2014;44:1337.
8. Therese SK, Vasudha VGT. Int J Inf Res Rev. 2015;2:261.
9. Shah AM, Rahim AA, Hamia SA, et al. Int J Electrochem Sci. 2013;8:2140.
10. Bujanovic B, Ralph SA, Reiner RS, et al. Materials. 2010;3:1888.
11. Higuchi T. Wood Sci Technol. 1990;24:23.
12. Ralph J, Lundquist K, Brunow G, et al. Phytochem Rev. 2004;3:29.
13. Tsuru T, Haruyama S, Gijutsu B. J Jpn Soc Corros Eng. 1978;27:573.
14. Benalli O, Larabi L, Traisnel M, et al. Appl Surf Sci. 2007;253:6130.
15. Li SH, Liu S, Colmenaresc JC, et al. Green Chem. 2016;18:594.
16. Marchessault RH, Coulombe S, Morikawa H. Can J Chem. 1981;60:2372.