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Green Approach to Corrosion Inhibition of Mild Steel by Lignin Sulfonate in Acidic Media

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Abstract: The inhibition effect of lignin sulfonate against corrosion for mild steel in acidic solution has been examined by means of FTIR (fourier transform infrared spectroscopy), FAA (flame atomic absorption) spectroscopy, SEM (scanning electron microscope), EDS (energy dispersive X-ray spectroscopy), and mass loss techniques. The results revealed that lignin is a beneficial inhibitor for mild steel corrosion in acidic medium. It has been further found that Langmuir adsorption isotherm is obeyed by the tested lignin's adsorption over the surface of mild steel. The range of inhibition efficiency (IE) in 2 mol·L^{-1} HCl was found to be 75.88%—87.88% for Reax 88A, 40.72%—60.32% for Reax 88B, and 54.32%—63.03% for Reax 100M, after immersed at 298 K for 24 h time.
Key words: mild steel; Fourier transform infrared spectroscopy; inhibition; adsorption; corrosion

The extensive use of mild steel in most industries and the problems associated with corrosion create an urgent need of protecting mild steel from the occurrence of corrosion within acidic media[1-3]. Corrosion has been a common and universal problem being faced by mild steel. There are a number of techniques which have been applied for ensuring the reduction of corrosion rate of metals. Out of all these techniques, the method of using corrosion inhibitor has found to be the most widely used technique. Many criteria should be taken into consideration for industrial and large scale for using inhibitors such as inhibitor's cost, its availability, toxicity, as well as environment friendliness. Therefore, in recent years, various types of organic[4-10] and natural materials, such as plants extracts that named as "green inhibitors", have gained significant attentions as a valuable and effectual inhibitor for corrosion for metal in the presence of acidic media[11-13]. Most of the studied organic inhibitors were comprised of sulphur, oxygen and nitrogen in their molecule[6,14-17].

Lignin is considered as a high-molecular mass and complex poly-phenolic polymer, which usually takes place within the cell walls of trees and plants[17], as well as some algae[18]. Different lignins were reported and identified in literatures, and were found to be cost effective for several different applications[19]. Previous investigations and their preliminary findings reveal that lignin is a good corrosion inhibitor and has the potential to be applied as a corrosion controlling agent in the presence of different systems[20,21]. In addition, lignin has found to be compatible with the environmental requirements. Lignin has found to be rich in the presence of phenolic and carboxylic functional groups. Potential complexation sites are constituted by the acidic moieties for metallic ions such as iron with the help of cation exchange mechanism[22-24]. The significant advantage of lignin over inorganic inhibitors is that lignin is capable of adsorbing over the surface of steel through the acid moiety's interaction with the film of metal hydroxide. Lignin also offers protective layer against oxygen or water, and it has found to be cheap and abundantly available constituent in the form of unwanted waste.

This work aims to examine the efficiency and effectiveness of several types of sulfonated lignin, which can play a role of corrosion inhibitors for mild steel when it is present in acidic solution. In order to carry out this research, different methods such as FTIR (Fourier transform infrared spectroscopy), EDS (energy dispersive X-ray spectroscopy), SEM

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(scanning electron microscope), FAA (flame atomic absorption) and mass loss methods were deployed. An attempt was also made to elucidate the effect of temperature on corrosion process, development of new phase over the surface of metal and chemical content, as well as morphology of corroded surface of metal.

1 Experimental

1.1 Materials

Coupons of mild steel (AISI 1010) were used throughout the experiments, with a thickness of 0.09 cm and the chemical composition (mass%) of C 0.08, Mn 0.32, P 0.027, S 0.03, Si 0.004 and Fe balance. The coupons of 3 cm×1 cm were formed through mechanical press cutting of the sheets. Additionally, several different grades of silicon carbide papers in the range of 100—800 grit were used for polishing the surfaces. After that, these coupons were washed thoroughly with deionized water. Subsequently, acetone was used for degreasing the coupons before using the coupons in each experiment.

Three types of lignin sulfonate named Reax 88A, Reax 88B, and Reax 100M were obtained from a paper manufacturing company (MeadWestvaco Corporation, USA). The physical characteristics of tested lignins are shown in Table 1. The preparation of reference solutions was carried out with the help of 1000 mg·L^{-1} of lignin sulfonate. It was further diluted in order to attain the concentration levels of 100, 300, 500 and 700 mg·L^{-1} in the presence of HCl (hydrochloric acid). The tested lignins are water-soluble anionic polyelectrolyte polymers, and the main building unit of these tested lignins is shown in Fig. 1. The structure shown in Fig. 1 does not specify the structure since lignosulfonates are complex mixtures; the purpose is to give a general idea of the structure of the main building unit of the tested lignin sulfonates.

Table 1 Physical characteristics of tested lignin sulfonate

Lignin	pH (15% by mass, aqueous solution, 298 K)	Degree of sulfonation (moles of $NaSO_3$/1000 g of lignin[1)])	Molecular mass/(g·mol^{-1})
Reax 88A	4.2	2.9	3100
Reax 88B	11.3	2.9	2900
Reax 100M	8.9	3.4	2000

Note: 1) Reported as obtained from MSDS.

1.2 Mass loss measurements

To carry out the experiment of mass loss, the mass

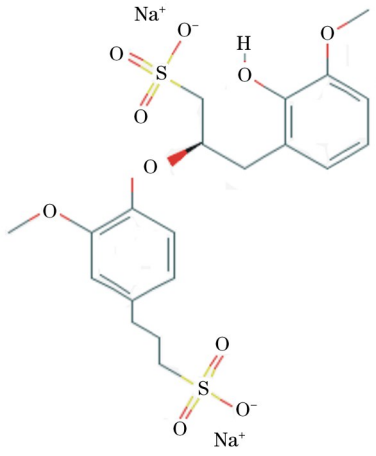

Fig. 1 Building unit of the tested sulfonated lignins

of pre-cleaned coupons of mild steel was measured. These coupons were then completely immersed vertically within test tubes containing 10.0 mL acidic solutions of different inhibitor concentrations. The temperature of 298 K in a thermostat bath (±0.1 K) was also maintained for carrying out this experiment. The test tube was covered to prevent any evaporation and contamination. The experiment of mass loss has been carried out through obtaining coupons of mild steel at different time (such as 6, 12, and 24 h). After each time, distilled water was used for washing coupons and bristle brush was further used for cleaning the coupon. Acetone was used for rinsing the coupon after cleaning process. These coupons were then dried and their mass was measured accurately by digital balance (±0.1 mg). The differences in coupon's mass after and before immersion within different test solutions were considered in order to carry out the experiment of mass loss. Triplicate was deployed for carrying out the experiments. The results which were obtained from the method of mass loss were deployed for calculating the rate of corrosion using Eq. (1):

$$C_R = \frac{m_1 - m_2}{A \times t} \quad (1)$$

where, C_R is the rate of corrosion, mg·cm^{-2}·h^{-1}; m_1 is the mass before the immersion of mild steel within test solutions, mg; m_2 is the mass after the immersion of mild steel within test solutions, mg; A is surface area of specimen, cm^2; and t is exposure time, h.

Corrosion inhibitor is considered as a chemical substance, the addition of which helps to efficiently decrease the rate of corrosion. The efficiency of inhibitor can be calculated through estimating inhibition efficiency. Similarly, the inhibition efficiency