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EFFECT OF RICE STRAW EXTRACT AND ALKALI LIGNIN ON THE CORROSION INHIBITION OF CARBON STEEL

(Kesan Ekstrak Jerami Padi dan Alkali Lignin Terhadap Perencatan Kakisan Keluli Karbon)

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Abstract

A paddy residue based corrosion inhibitor was prepared by treating finely powdered rice straw with aqueous ethanol under acid catalyst (0.01M H_2SO_4). Commercial alkali lignin was obtained from Sigma-Aldrich. Prior to the corrosion test, the extraction yield and alkali lignin was characterized via FTIR to determine the functional group. The effect of paddy residue extract and commercial alkali lignin on the corrosion inhibition of carbon steel in 1M HCl was investigated through the weight loss method, potentiodynamic polarization technique and scanning electron microscopy (SEM). The corrosion inhibition efficiency of the extract and alkali lignin at different immersion times (3h, 24h and 42h) was evaluated. The results show that the paddy waste extract exhibited lesser weight loss of carbon steel in the acidic medium in comparison to the commercial alkali lignin, suggesting that the paddy residue extract is more effective than the commercial alkali lignin in terms of its corrosion inhibition properties. The results obtained proves that the extract from paddy residue could serve as an effective inhibitor for carbon steel in acidic mediums.

Keywords: Rice straw extract, corrosion, carbon steel, inhibition

Abstrak

Perencat kakisan dari sisa padi disediakan dengan merawat serbuk halus jerami padi dengan akues etanol di bawah pengaruh pemangkin asid (0.01M H_2SO_4), sementara alkali lignin komersial diperolehi daripada Sigma-Aldrich. Sebelum ujian kakisan dijalankan, hasil ekstrak dan alkali lignin komersial telah dicirikan melalui FTIR untuk mengetahui kumpulan berfungsi bahan-bahan tersebut. Kesan ekstrak dari sisa padi dan alkali lignin komersial terhadap perencatan kakisan keluli karbon dalam 1M HCl ditentukan dengan kaedah kehilangan berat, teknik pengkutuban potensiodinamik dan mikroskopi pengimbasan elektron (SEM). Kecekapan perencatan kakisan ekstrak dan alkali lignin ditentukan untuk masa rendaman yang berbeza (3j, 24j dan 42j). Keputusan menunjukkan bahawa ekstrak sisa padi mempamerkan kurang kehilangan berat keluli karbon dalam media asid berbanding alkali lignin komersial. Ekstrak dari sisa padi didapati lebih berkesan berbanding alkali lignin komersial dari segi sifat perencatan kakisan. Keputusan yang diperolehi membuktikan bahawa ekstrak dari sisa padi boleh bertindak sebagai perencat yang berkesan bagi keluli karbon dalam media asid.

Kata kunci: Ekstrak jerami padi, kakisan, keluli karbon, perencatan

Introduction

Recently, researchers have been focusing their efforts in the pursuit to replace synthetic corrosion inhibitors with inhibitors obtained from natural substances. This interest has been in high demand due to the fact that naturally sourced corrosion inhibitors are safe, readily available, cheap, ecologically friendly, biodegradable and sourced from renewable materials [1-2]. Various studies have reported that extracts of natural ingredients can slow down and inhibit corrosion, due to the presence of oxygen compounds, sulphur and nitrogen that can help in the process of corrosion inhibition [3-5]. Previous literature has shown that natural material such as Henna leaf extract [6], *Aloe Vera* extract [7], mangrove bark [8], natural honey and black radish juice [9] are effective inhibitors for metal in aggressive solutions.

This study focuses on comparing the corrosion inhibition properties of rice straw extract and commercial alkali lignin. Rice straw was chosen because it is a waste management issue in Malaysia, causing problems such as pollution that can affect human health. This represents a huge missed oppurtunity, especially when these residues can be converted into substances that are beneficial to the community. The inhibition behaviour of both materials on carbon steel was determined in a 1M HCl solution, via the weight loss method and potentiodynamics polarization technique.

Materials and Methods

Rice straw samples were obtained from a private paddy field in Kedah, Malaysia. The rice straw was dried for 16 hours in an oven at 60°C and ground into powder. The dried and ground rice straw was extracted by a solvent extraction method in a aqueous ethanol (ethanol/water, 60/40) with stirring acid catalyst (0.01M H_2SO_4) at 50-60°C for 12h. The ethanol used was then evaporated, leaving behind a black liquor. This black liquor was then transferred into a petri dish and dried in the oven at 100°C for 6 h to obtain an extract product. The extract left in the petri dish was then scraped of the petri surface, producing the final product in the form of a black powder. Meanwhile, the commercial alkali lignin obtained from Sigma-Aldrich was used as received. The powder extracted from rice straw and the commercial alkali lignin was analysed using a Perkin Elmer Spectrum 400 FT-IR/ FT-NIR & Spotlight 400 Imaging System in a wavelength range of 400 to 4000 cm^{-1}, to recognize the functional groups present in the extract powder and the commercially obtained alkali lignin. To study the corrosion inhibition behaviour of the rice straw extract and commercial alkali lignin, an arsenal of analytical methods were employed. The weight loss method was used in the corrosion test. Carbon steel SAE 1045 samples with the following composition (C=0.45%, Mn=0.75%, P=0.04% max, S=0.05%) were used. This carbon steel was mechanically cut into smaller test pieces with a diameter of 16mm and thickness of 1mm. Prior to the weight loss test, the specimens were abraded with a series of silicon carbide papers (grade 400, 600, 800 and 1200) before being washed with distilled water, degreased with acetone, dried and weighed.

For the preparation of the corrosion inhibitor solution, a 1M hydrochloric acid solution was first prepared by dilution of analytical grade 37% HCl with distilled water. A corrosion inhibitor solution containing the rice straw extract and commercial alkali lignin was prepared in a 100ml of 1 M hydrochloric acid. Both inhibitors were dissolved at a concentration of 1500ppm. The 1M HCl solution without inhibitors was used as the blank for comparison. Weight loss of the carbon steel test pieces were determined at varying immersion times (3h, 24h and 42h) at room temperature. At each specified time interval, the specimens were taken out of the test solution, rinsed with distilled water, dried and weighed again. The weight loss was measured in milligrams. The test was carried in triplates to obtain accurate results and the mean of weight loss was recorded [10].

Polarization measurements were carried out using a computer-controlled potentiostat (model K47 Gamry framework). Three different types of electrodes were used a saturated calomel electrode (SCE) as reference, the working electrode was carbon steel and platinum wire was the counter electrode. The working electrode surface area used in this study was [illegible] cm^2. The surface of carbon steel was abraded successively using silicon carbide paper 400, 600, 800 and 1200 grade. The ground surface was degreased with acetone and washed with distilled water before being used in the experiment. Before each polarization measurement, the working electrode was left idle for 30 minutes to achieve a steady state. The experiments were performed using a scanning rate of 1.0 mV s^{-1}. All the measurements were done at room temperature.

Scanning electron microscopy SEM analysis was carried out to study surface morphology of the untreated and treated carbon steel with the rice straw extract and commercial alkali lignin corrosion inhibitors.

Results and Discussion

FTIR analysis

FTIR spectroscopy displays interesting features such as high signal-to-noise ratio, high sensitivity and selectivity, accuracy, mechanical simplicity, short analysis time and small amount of sample required for the analysis [11]. Figure 1 illustrates the FTIR spectra obtained for the rice straw extract and commercial alkali lignin. Table 1 displays the chemical bonds assigned to the FTIR absorption bands of the rice straw extract and commercial alkali lignin. The observed peaks for the extract exhibited signal peaks for functional groups such as hydroxyl (-OH), methoxyl (-OCH_3), methyl (CH_3) and aromatic rings that can retard the corrosion process. Organic compounds such as hydroxyl (-OH), methoxyl (-OCH_3) and methyl (CH_3) are known to be electron donating groups that can play a role as a good inhibitor for metal corrosion in acidic media [12]. The compound will adsorb onto the metal surface. As a result, it reduces the exposed surface area from being attacked by the aggressive acidic media [1]. The typical signal peaks of lignin for both the extract and commercial alkali lignin was also present at wavelengths of 1514 cm^{-1} and 1500 cm^{-1}, respectively. The cellulose peak can be observed at a wavelength of 1419 cm^{-1} for commercial alkali lignin, but was absent in the rice straw extract. The presence of hemicellulose at 1237 cm^{-1} for the extract and 1210 cm^{-1} for commercial alkali lignin as reported by others [13-14]. As can be seen from Table 1, the rice straw extract shows an observable peak at a wavelenghts numbers of 1324.00 cm^{-1}, which indicates the presence of syringyl compound. However, the commercial alkali lignin does not show any peaks in this range of wavelengths. The existence of syringe could be the reason for the capability of the corrosion inhibitor solution to reduce the corrosion rate of metals by strongly attracted to the positively charged electrode surfaces [15].

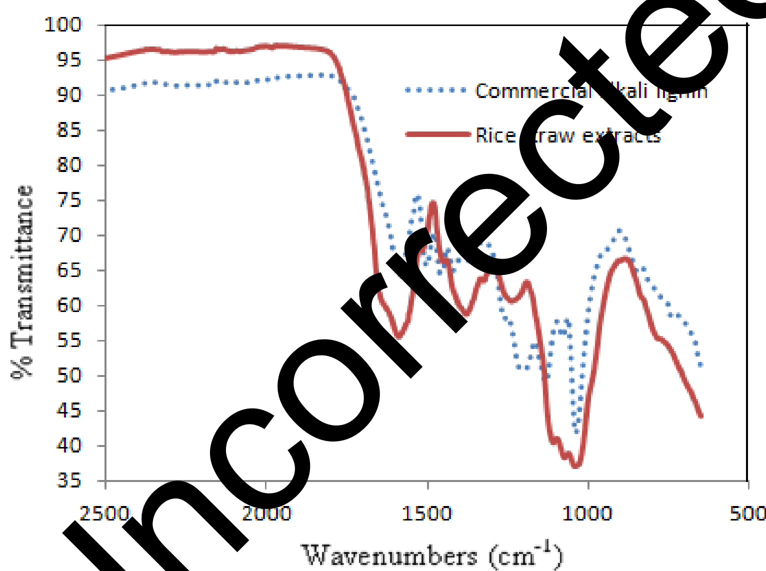

Figure 1: The FT-IR spectrum for rice straw extract and commercial alkali lignin

Weight loss measurements

Corrosion process can be investigated by using the simplest and long-established method that called weight loss analysis. The differences in weight of specimens before treated and after treating with inhibitor can be expressed as corrosion rate [19-20]. The corrosion rate and inhibition efficiency can be calculated by the formula Equation 1 and 2 given below:

$$Corrosion\ rate\ (CR, mpy) = \frac{534W}{DAT} \tag{1}$$

$$Inhibition\ efficiency\ (IE, \%) = \left(1 - \frac{CR2}{CR1}\right) x\, 100 \tag{2}$$

where W = weight loss in mg, D = density of the specimen in unit g/cm^3, A = area of specimen in inch^2, T = exposure time in hour meanwhile CR_1 and CR_2 are the corrosion rate in the absence and presence of inhibitors.

Table 1: Peak FTIR spectrum for rice straw extract and commercial alkali lignin

Wavenumber range (cm^{-1})	**Observe peak (cm^{-1})**		**Peak assignment**
	Rice straw extract	**Commercial alkali lignin**	
1600-1550	1590.34	1587.50	Aromatic skeletal vibrations [16-17].
1550-1500	1514.31	1500.59	C=C stretching of aromatic ring in lignin.
1500-1450	1450.88	1459.43	Assymmetric C-H deformations, C-H and C-O bending or stretching frequencies [18].
1450-1400	-	1419.92	C-H bending of methyl and methylene groups.
1400-1350	1379.84	1373.56	Weak C-O stretching, C-H symmetric and asymmetric deformation.
1350-1300	1324.00	-	C-O stretching, Syringyl ring breathing with C=O stretching [18].
1250-1200	1237.52	1210.68	Pure hemicellulose
1150-1050	1107.92 1072.24	1131.59 1079.70	Aromatic C-H deformation of syringyl unit β(1-3) polysaccharide.
1050-1000	1040.50	1038.80	C-O, C=O, C-C-O vibrational stretching C-OH bending, primary –OH group.
800	-	848.23	C-H bending of syringyl units.
700	786.78	739.20	Asymmetric bending of HCCH group.

The data obtained for the corrosion behaviour of carbon steel in 1M HCl containing rice straw extract and commercial alkali lignin with various immersion times are presented in Table 2. It represents that the weight loss percentage in the absence and presence of the rice straw extract. At the time of carbon steel being exposed to the HCl media increased, the weight loss increases. Compare with commercial alkali lignin, the extract solution from rice straw produced the lowest weight loss. The lowest weight loss indicates that the rice straw extract could be served as an effective inhibitor of carbon steel in acidic medium. The inhibition process is the result of an adsorption of the inhibitor molecule on the carbon steel surface where rice straw extracts solutions act as an adsorptions inhibitor. The reaction between inhibitor and carbon steel surface could limit the occurring of corrosion processes. The comparative value of weight loss of carbon steel can be seen clearly in Figure 2.

Table 2: The percentage of weight loss for rice straw extract and commercial alkali lignin in 1M HCl with different immersion time

Corrosion inhibitor solution	**Weight loss percentage (%)**		
	3 hour	**24 hour**	**42 hour**
1M HCl	9.9	57.8	95.8
1M HCl + 1500ppm Commecial alkali lignin	4.1	24.5	46.7
1M HCl + 1500ppm rice straw extracts	0.3	0.6	0.7

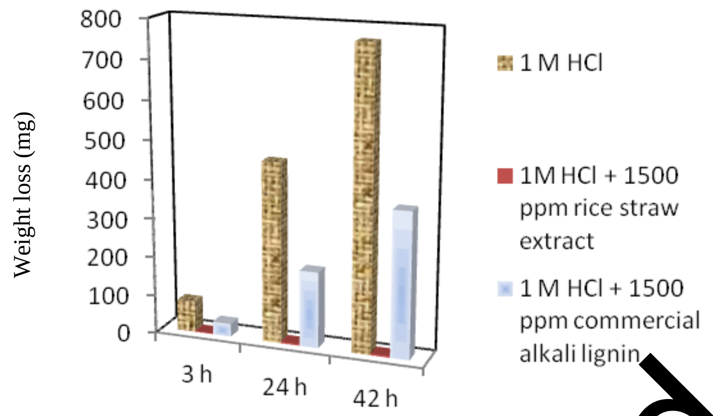

Figure 2: The weight loss of carbon steel in 1M HCl solution for rice straw extract and commercial alkali lignin at different immersion time

Potentiodynamics polarization technique

Polarization behaviour for carbon steel in 1M HCl in the absence and presence rice straw extract and commercial alkali lignin are shown in Figure 3. The values of corrosion or corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope b_c, anodic Tafel slope b_a and inhibition efficiency (E%) are collected in Table 3. From Table 3, the corrosion potential for 1M HCl is -404mV. When carbon steel is immersed with the presence of 1500ppm commercial alkali lignin, there is no changed in corrosion potential value. It reveals that the addition of commercial alkali lignin may not give an influence into corrosion potential. Meanwhile, the corrosion potential for extract of rice straw shifts to -414mV. It is clearly shown that there is a shift towards cathodic region in the values of corrosion potential. In the literature, it has been reported that if the displacement in E_{corr} is >85V with respect to E_{corr}, the inhibitor can be seen as a cathodic or anodic type, and if the displacement in Ecorr is <85, the inhibitor can be seen as mixed type. In our study the maximum displacement in Ecorr value was 10mV towards cathodic region, which indicates that rice straw extract is mixed type inhibitors [21-22].

Table 3: Tafel polarization parameters for the corrosion of carbon steel in 0.5 M HCl solution for rice straw extract and commercial alkali lignin

System/ Inhibitor	**I_{corr} (A cm^2)**	**E_{corr} (mV)**	**b_c (mVdec-^{1})**	**b_a (mVdec-^{1})**	**Rp (kΩ cm^2)**	**CR (mmpy)**
1M HCl	3.0×10^{-3}	-404	183	140	1.2×10^1	34.43
1500 ppm commercial alkali lignin	1.9×10^{-3}	-404	197	124	1.7×10^1	22.85
1500 ppm rice straw extract	6.5×10^{-5}	-414	101	74	2.8×10^1	0.76

Surface analysis on the corroded coupons

Scanning electron microscopy (SEM) of the polished surface of carbon steel exposed for 24 hours in 1M HCl solution in the absence and presence of 1500ppm rice straw extract and commercial alkali lignin are shown in Figure 4. By comparison of SEM images at the same magnifications, there was a rough surface of carbon steel in the presence of commercial alkali lignin and smooth surface with deposits extract in presence of the rice straw extract. Protective layer can be observed on the corroded surface. The rice straw extract forms a protective layer by physical adsorption process. It proved again the inhibiting rice straw extract against corrosion of carbon steel in 1M HCl solution is better than commercial alkali lignin.

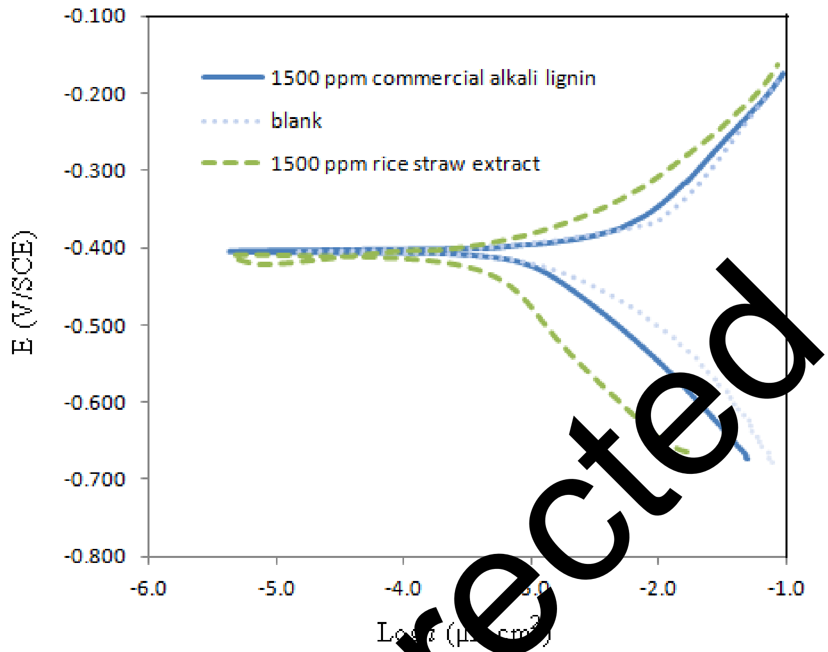

Figure 3: Tafel polarization curves for carbon steel in 1M HCl solution containing rice straw extract and commercial alkali lignin

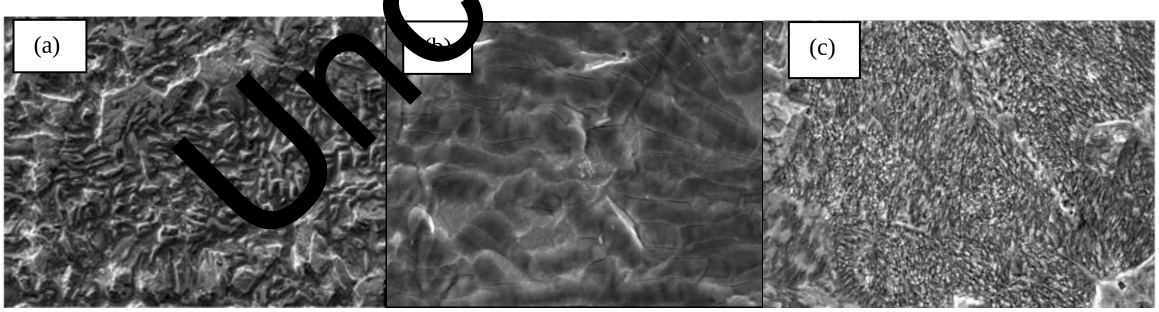

Figure 4: SEM morphology of carbon steel sample, (a) absence inhibitor, (b) in presence of commercial alkali lignin (c) in presence of rice straw extract in 1M HCl solution for 24h

Conclusion

Both commercial alkali lignin corrosion inhibitor and extract yields from rice straw can prevent carbon steel from corrosion attack but rice straw extract showed a better efficiency as corrosion inhibitor. This behaviour may occur due to the existence of syringyl compound that obtained from FT-IR results.

Acknowledgement

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